

Prediction of Properties of Fluids by Molecular Simulation Techniques

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Prediction of Properties of Fluids by Molecular Simulation Techniques

*Thesis submitted in partial fulfillment
of the requirements of the degree of
Master of Technology Dual Degree
in*

***Chemical Engineering
(Specialization: Chemical Engineering)***

by

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*based on research carried out
under the supervision of
Prof. Basudeb Munshi*



May, 2016

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Supervisor's Certificate

This is to certify that the work presented in the thesis entitled *Prediction of Properties of Fluids by Molecular Simulation Techniques* submitted by *Sangita Swapnasrita*, Roll Number 711CH1156, is a record of original research carried out by her under my supervision and guidance in partial fulfillment of the requirements of the degree of *Master of Technology Dual Degree in Chemical Engineering*. Neither this thesis nor any part of it has been submitted earlier for any degree or diploma to any institute or university in India or abroad.

Basudeb Munshi

Dedication

Dedicated to Prof. Basudeb Munshi and Prof. Sandip Khan.

Sangita Swapnasrita

Declaration of Originality

I, *Sangita Swapnasrita*, Roll Number *711CH1156* hereby declare that this thesis entitled *Prediction of Properties of Fluids by Molecular Simulation Techniques* presents my original work carried out as a postgraduate student of NIT Rourkela and, to the best of my knowledge, contains no material previously published or written by another person, nor any material presented by me for the award of any degree or diploma of NIT Rourkela or any other institution. Any contribution made to this research by others, with whom I have worked at NIT Rourkela or elsewhere, is explicitly acknowledged in the dissertation. Works of other authors cited in this dissertation have been duly acknowledged under the section “Reference”. I have also submitted my original research records to the scrutiny committee for evaluation of my dissertation.

I am fully aware that in case of any non-compliance detected in future, the Senate of NIT Rourkela may withdraw the degree awarded to me on the basis of the present dissertation.

May 23, 2016
NIT Rourkela

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Abstract

Chemical Engineering Thermodynamics and Transport Phenomena are driven by the need to have physical description of phase properties for pure components and fluid mixtures. Thus, a number of high quality experimental methods and simulation methods have been devised for many mixtures over the years. However, some systems like alkanes, alcohol, water and mixtures are very difficult to model. A lot of these models are phenomenological and the modelling techniques available are still not accurate for the determination of parameters. Some models are centric to the specific data range and hence cannot be extrapolated. Eventually if we develop a mathematical model which is a good one then it can offer insights to the experimentalists and assist in the interpretation of the results.

Large scale simulations are a good alternative to the conventional physical modelling techniques. Computer simulations provide essentially exact results for statistical mechanics problems which would otherwise have to be approximated or even be quite intractable. A number of recent studies have expanded the range of systems for which properties can be studied with the help of simulation. There are two main classes of computer simulations, Monte Carlo (MC) simulations and Molecular Dynamics (MD) simulations. Monte Carlo simulation is an automated numerical technique that allows individuals to represent risk in quantitative analysis and choice making. Molecular dynamics, on the other hand, are used to simulate coupled differential equations as in case of equations of motion. Hence, it can be used to study the equilibrium and non- equilibrium properties of matter or mixtures as close to real physical systems as possible.

Literature is rich with the experimental data about the various transport properties of alkanes, alcohols and water. A few research works are available where molecular simulation techniques were used to model such fluids and predict the properties. However, the literature data is scanty when it comes to lower alkanes and also mixture of alkanes. In the present study, Green-Kubo formulae have been used to predict the viscosity for such lower alkanes at a set of temperatures and at different box sizes.

In the present study, both MC and MD simulation technique have been applied to study the properties of a basic fluid system of Argon in the temperature range of 150 to 700 K and reduced density range of $0.05 \leq \rho \leq 1.0$. The average of the physical properties like potential energy and pressure was calculated in MATLAB environment. The standard deviation for MC and MD simulation was found out to be 0.502 and 0.227 respectively.

Then we gradually moved to complex fluids such as alkanes, water and alcohol. So, MC simulations was carried out to predict the average energy and density of alcohols, alkane and three different water models and the results are successfully validated with the literature data with a standard deviation of 0.054.

MD simulation was used to predict the viscosity and average density of ethane, propane, butane and isobutene at different temperatures and different box sizes. The viscosity of a mixture of ethane and propane in the ratio 1:1 was also studied at different parameters. The effect of variation of temperature and number of molecules in the box on the accuracy of the prediction of viscosity was also studied.

Keywords: Viscosity; Monte Carlo simulation; Molecular Dynamics simulation; LAMMPS; density.

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Nomenclature

$P_{reduced}$	Reduced pressure
V	Total volume
$T_{reduced}$	Reduced temperature
μ	Chemical potential, dipole moment
ρ	Density
MC	Monte Carlo
MD	Molecular Dynamics
LJ	Lennard Jones
r_{ij}	Distance between and atom
σ, ϵ	Length and energy parameters
N	total number of atoms
$\langle \rangle$	Time Average of the property
η	Viscosity
U_{tot}	Total potential
U_b	Bending potential
U_t	Torsion potential
U_{LJ}	Lennard Jones potential
θ_i, θ_0	Bond angle, equilibrium bond angle
ϕ_i	Dihedral angle
c_i	Torsion potential coefficients
λ	Rescaling factor
L	Simulation Box size
r_c	Cut- off radius
k_B	Boltzmann constant
m	Mass of the molecule
t	Time step
E	Energy
U	Potential Energy
$f_{friction}$	Frictional force
γ	Shear rate
v_i	Velocity of the molecule in ith direction

Chapter 1

Introduction

Chemical Engineering Thermodynamics and Transport Phenomena are driven by the need to have physical description of phase properties for pure components and fluid mixtures. The history is rich with theoretical and experimental methods to study the state of matter. Theoreticians and experimentalists have tried to replicate fluid models with simple physical models. However, such methods are time-consuming and the obvious effects of gravity cannot be neglected. Thus, there was the need to develop a mathematical model and do the analysis with the help of computer. The very first simulation was done by Metropolis[1] in 1953 which is now known as Monte Carlo simulation using highly idealised models for molecules such as hard spheres or discs. Then, Wood and Parker[2] developed a model by calculating interaction between molecules using Lennard Jones potential. This enabled to compare the results of simple LJ fluids like argon with experimental values. MD technique was first devised by Alder and Wainwright[3] in 1957 to calculate dynamic properties for many-particle systems. It assumed perfectly elastic collisions between the molecules and it was possible to solve the equations of motion without approximations but within the range of the accuracy imposed by the machine. Several years later, Rahman[4] in 1964 perfected a MD system to solve equations of motion for LJ particles. Since then, several studies have been done on LJ particles and have even proceeded to predict the dynamic properties for complex fluids and even multi-component systems.

The main obstacle in performing a simulation is the availability of a good force field. Several good force fields are being developed for specific types of mixtures like OPLS[5]–[8] (Optimized potential for liquid simulation), TraPPE[9]–[11] (Transferrable potential for phase equilibria) and several other variations.

Several open source software have also been developed like GROMACS[12], NAMD[13], DL-POLY[14] with integrated force fields to ease the task of writing humongous codes. The first two software are the typically used for biological systems, and the last one is mainly used for polymeric systems. Other software are also available like AMBER,CHARMM[15], [16], X-PLOR and LAMMPS[17] for MD simulation. The Lennard-Jones fluid[18] model has been the bench mark for all these software. It is an oversimplified fluid model but it captures the essential physics of simple fluids. An attempt has been made to replicate such

a fluid namely Argon by the means of Monte Carlo simulation and Molecular Dynamics simulation.

1.1 MONTE CARLO SIMULATION

Monte Carlo [19] is a set of computational algorithm based on random sampling to obtain results based on probability of occurring. Monte Carlo is used in broad class of problems: numerical integration, generating and optimisation and generally draws result from probability distribution.

Monte Carlo simulation is an automated numerical technique that allows individuals to represent risk in quantitative analysis and choice making. This method is utilized by experts as a part of such broadly unique fields as finance, physical sciences, engineering, computational biology, computer graphics, applied statistics, design and visuals, artificial intelligence, business and many more. The scope of the simulation is limitless and varied. Thus, it is one of the most extensively used procedures. The procedure was initially utilized by researchers dealing with the atom bomb; it was named for Monte Carlo, the Monaco resort town prestigious for its club. Since its beginning in World War II, Monte Carlo reproduction has been utilized to show an assortment of physical and calculated systems.

Monte Carlo simulation employs stochastic methods to generate a large number of samples, with each sample guided by a random number. There lies the flexibility of MC simulation. Basic generators are available in FORTRAN90, MATLAB or C to generate random number. The general procedure followed in a MC simulation is:

- Generate a “new” trial configuration by making a random perturbation.
- Accept the new configuration based on the ratio of probabilities for the new and old position (Metropolis algorithm).
- If the trial is rejected, then the old configuration is taken as the new one.
- This is repeated for many steps accumulating sums for averages. Acceptance rate is checked in between the simulation to ensure that the system is being perturbed. For typical systems, acceptance rate is about 50% and it may be reduced to lower values for hard spheres.

1.2 MOLECULAR DYNAMICS SIMULATION

Molecular Dynamics (MD) simulation was introduced by Alder and Wainwright[3] in the late 1950s’ to study hard spheres. The first simulation was done by Rahman and Stillinger in 1974- simulation of liquid water[4]. Since then, numbers of simulation techniques have

been employed. A lot of specialised software have been developed including NAMD[13], GROMACS[12], LAMMPS[17], etc. to study particular problems. MD simulations are being used to study enzymatic reactions[19]–[22], protein structure[22],[23], liquid-liquid equilibrium[24], [25] as well as experimental procedures such as X-Ray crystallography and NMR structure determination.

In a MD simulation, the association between microscopic and macroscopic properties is made by means of statistical mechanics which gives the equation of motion that relate macroscopic properties to the distribution and movement of the molecules and atoms of the N-body system. MD provides the means to solve these equations and evaluate the results. One can study thermodynamic as well as kinetic properties with the help of MD simulations.

1.3 SOFTWARE USED

- i. **MATLAB:** Matlab (Matrix laboratory) is a fourth generation programming language developed by Mathworks to implement algorithms, manipulate matrix, plot function etc.
- ii. **LAMMPS:** LAMMPS[17](Large-Scale Atomic/Molecular Massively Parallel Simulator) is an open source MD program developed by Sandia National Laboratories.
- iii. **VMD:** VMD[26] (Visual molecular dynamics) is a tool to analyse the results of molecular dynamics simulations developed by University of Illinois.

1.4 OBJECTIVES

In this report, both MC and MD simulation have been performed to calculate properties like average energy, average pressure, average density and average viscosity. Thus the objectives of the work are divided into two sections:

- I. To find the equilibrium properties like average energy and density of argon, water (SPCE, TIP3p and TIP4p), alkane (methane, propane and butane) and alcohol (ethanol and propan-1-ol) by Monte Carlo simulation
- II. To find the properties of argon, alkane (ethane, propane and butane) and a mixture of alkane (ethane and propane) by Molecular Dynamics simulation

1.5 ORGANISATION OF THE REPORT

Chapter 1 deals with the introduction to Monte Carlo simulation and Molecular Dynamics simulation.

Chapter 2 deals with literature survey on Monte Carlo and Molecular Dynamics simulation of different types of fluid systems.

Chapter 3 deals with the results and discussions of the work. In this chapter, there are sections on the results obtained from the various simulations.

Chapter 4 deals with the conclusion and future scope of the project work.

Chapter 2

Literature Survey

The literature review has been sectioned into three parts. The first involves the basic understanding of the terminology that is frequently used in molecular simulations. The second part includes the literature review done on Monte Carlo simulation and the third part of this chapter revolves around the research work done previously on Molecular Dynamics.

2.1 BASIC UNDERSTANDING OF MOLECULAR SIMULATION TECHNIQUES

This section includes a description of terms that frequently occur in a molecular simulation.

2.1.1 Lennard Jones Fluid

Lennard-Jones (LJ) potential model is one of the very important models for obtaining properties like phase co-existence, melting point and various other transport properties of simple fluids. The LJ potential is given by

$$U_{LJ} = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (2.1)$$

where ϵ is the LJ well depth and σ is the LJ atomic diameter.

The LJ potential term consists of the attractive forces of the form $(1/r^6)$ and steep repulsive forces of the form $(1/r^{12})$. The parameters σ and ϵ when chosen appropriately give a reasonable description for the properties of argon by computer simulations. These calculations are very tedious and use up 90% of the total computation time. In order to reduce the pair interaction computation time in the simulation the potential is truncated at r_c , the cut-off radius, usually less than $L/2$ where L is the simulation box size.

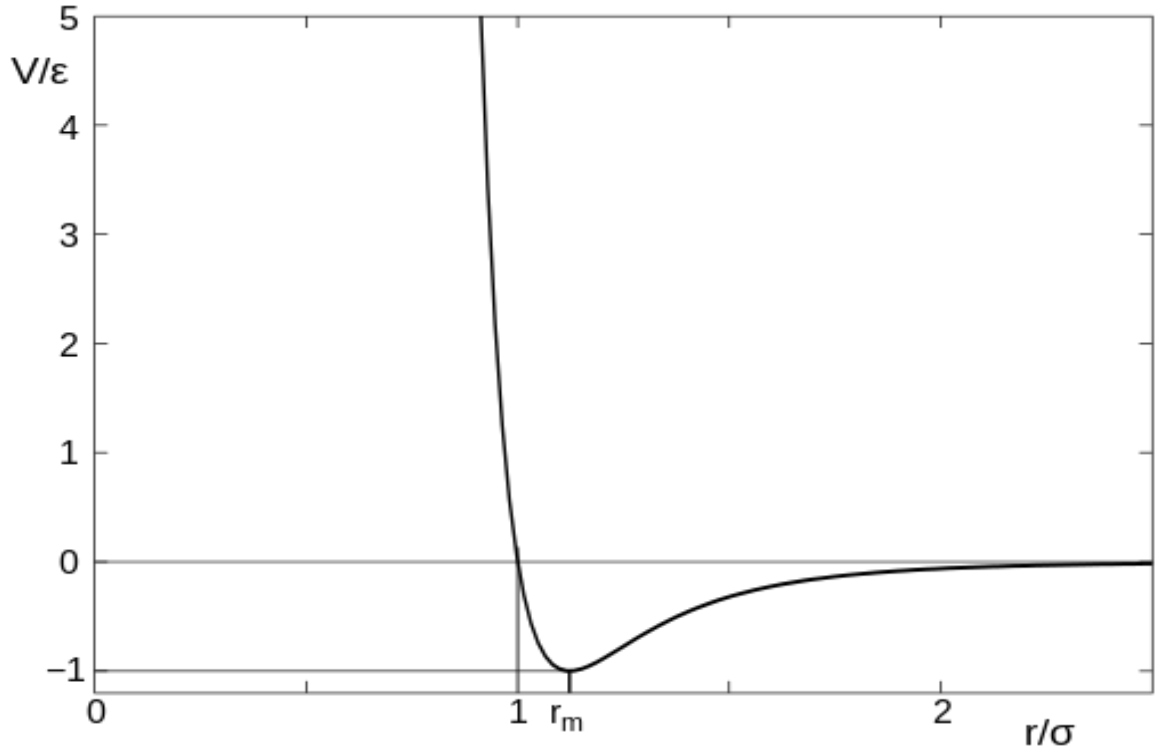


Figure 2.1: LJ Potential in reduced units where r_m is the cut-off radius and V is the potential energy.

2.1.2 Cut-Off Radius

Cut- off radius is the radius at which the potential is usually truncated. The value of cut-off radius is usually fixed at half the box size. Although this kind of truncation reduces computation time, it may sometimes lead to large error. Instead long range correction or tail correction are obtained for $r > r_c$. This leads to the following tail correction results for pressure and potential:

$$P_{lrc} = \frac{32}{9}\pi\rho' \left[\left(\frac{\sigma}{r_c} \right)^9 - \frac{3}{2} \left(\frac{\sigma}{r_c} \right)^3 \right] \quad (2.2)$$

$$U_{lrc} = \frac{8}{9}\pi\rho' \left[\left(\frac{\sigma}{r_c} \right)^9 - 3 \left(\frac{\sigma}{r_c} \right)^3 \right] \quad (2.3)$$

2.1.3 Ensemble

A specification of all atom positions and momenta subject to one extensive constraint like fixed total energy, fixed volume or fixed total number of molecules is known as an ensemble. Different ensembles commonly used in molecular simulations are NPT-isothermal isobarical (constant N, P and T), NVT-canonical (constant N, V and T), NVE-microcanonical (constant N, V and E), μ VT-grand canonical (constant μ, V and T) and NPH (constant N, P and

enthalpy).

In the present study, we have used NVT and NPT ensembles for the MC simulations and NVE, NPH and NPT ensembles for MD simulations.

2.1.4 Periodic Boundary Conditions

It is impossible to contain a system within a box. Hence, most of the times periodic boundary conditions (PBCs) are imposed to enhance the finite size effects and to determine the apparent effect of boundary on system properties.

It considers the nearest image to calculate the distance. The molecules going outside the box are ignored and their periodic images are considered to move inside the box to maintain the box density. However, this results in increased number of calculations and as a result the computation time increases. Thus, the cut-off radius is used to limit the sphere of calculation (figure 2.2). Cubic, hexagonal, truncated octahedron (3D), rhombic dodecahedron (3D) are the commonly used PBCs.

In the present study, we have performed all the simulations on a cubic periodic box.

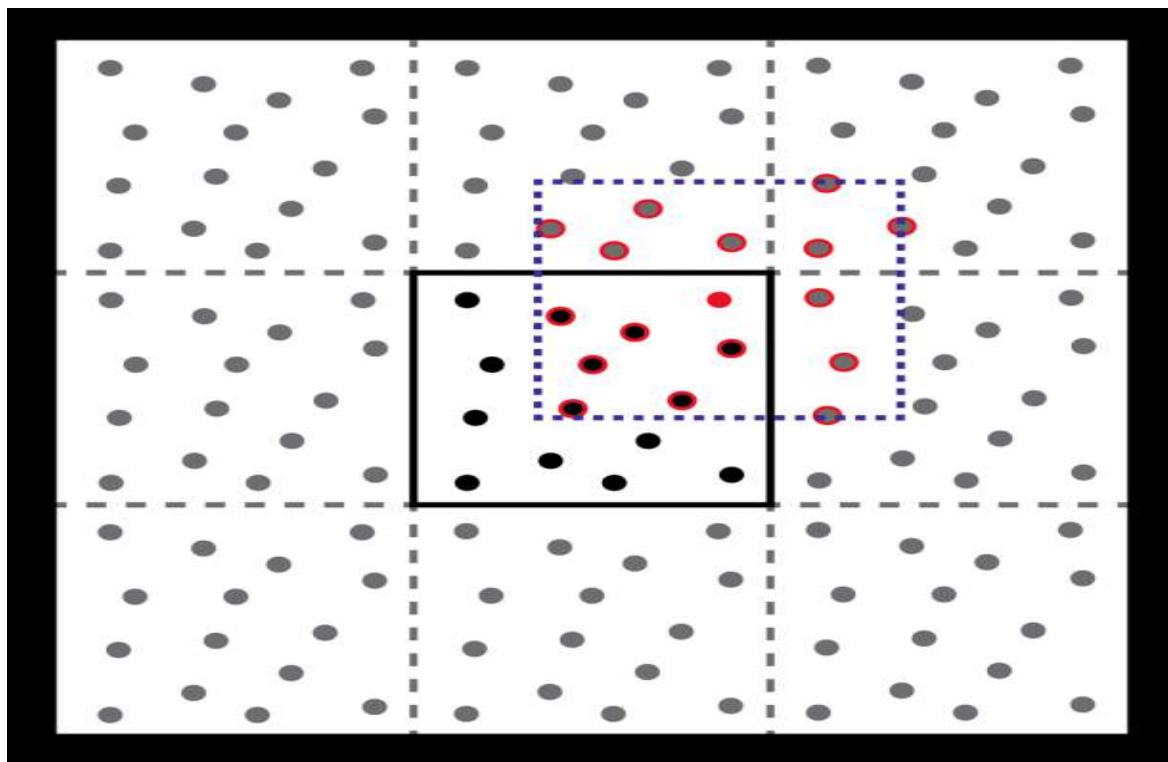


Figure 2.2: Cubic PBC [48].

2.1.5 Reduced Units

For simplification of calculation for a LJ fluid, reduced units are considered for the properties. All quantities are made unitless. LAMMPS sets the value of quantities such

as mass, sigma, epsilon and Boltzmann constant as 1. The following formulae are used to convert the reduced unit to the physical quantities.

$$\rho_{reduced} = \frac{N}{V} \cdot \sigma^3 \quad (2.4)$$

$$T_{reduced} = \frac{k_B T}{\epsilon} \quad (2.5)$$

$$t_{reduced} = t \sqrt{\frac{\epsilon}{m \sigma^3}} \quad (2.6)$$

$$r_{reduced} = \frac{r}{\sigma} \quad (2.7)$$

$$E_{reduced} = \frac{E}{\epsilon} \quad (2.8)$$

$$P_{reduced} = \frac{P \sigma^3}{\epsilon} \quad (2.9)$$

2.1.6 Velocity

Velocities for the particle are generally given as input to a molecular simulation. The velocity generally follows a Maxwell or Gaussian distribution such that the average velocity is set to zero. Then the velocity is rescaled to the required temperature.

$$\lambda = \sqrt{\frac{T}{T_{inst}}} \quad (2.10)$$

where λ is the velocity rescaling factor, T is the required temperature and T_{inst} is the instantaneous temperature.

2.1.7 Thermostats and Barostats

Thermostats

The above discussed approach to temperature control by velocity rescaling works but it has certain disadvantages. When the particle moves to positions where the potential energy is lower than instantaneous potential energy there is a considerable gain in the kinetic energy to keep the total energy constant. This sometimes leads to runaway results with higher temperatures than required. This makes controlling temperature complicated at times. Temperature explicitly controlled however does not have the previous shortcomings. Thermostats are used to directly control temperature instead of indirect control as in case of velocity rescaling.

BERENDSEN THERMOSTAT

The Berendsen thermostat assigns a time scale rather than temperature scaling at each time step. This is equivalent to the simulation box being coupled to a weak heat bath.

$$\lambda^2 = 1 + \frac{\delta t}{\tau} \left(\frac{T}{T_{inst}} - 1 \right) \quad (2.11)$$

where τ is the transfer function of the bath usually 0.1–0.4ps for $\delta t = 1fs$.

ANDERSON THERMOSTAT

The Anderson thermostat considers random collision with an imaginary heat bath at desired temperature at a collision frequency (not shorter than the time scale of molecular motions). Each component of the velocity is reassigned a velocity randomly out of the following Maxwell- Boltzmann distribution.

$$\Psi(v_{i,j}) = \left(\frac{m_i}{2\pi k_B T} \right)^{\frac{1}{2}} \exp\left(-\frac{m_i v_{j,i}^2}{2k_B T} \right) \quad (2.12)$$

where m_i is the mass of the i^{th} particle, k_B is the Boltzmann constant and $j = x, y$ and z .

BAROSTATS

It is often desired to maintain the simulated systems at constant temperature and pressure. Barostats are used for the purpose of maintaining pressures of system by manipulating the volume of the system. There are different kinds of barostats and they are similar to their thermostat counterparts.

VOLUME RESCALING

The desired pressure is maintained by rescaling the volume of the simulated box at definite time intervals.

BERENDSEN BAROSTAT

The system is coupled to a weak pressure bath and the system is assigned a time scale as well.

ANDERSON BAROSTAT

The system is coupled to an imaginary pressure bath similar to an Anderson Thermostat.

2.1.8 Langevin Dynamics

Implicit solvation is employed in many systems that are simulated. When the solvent atoms are removed, the solute particles no longer experience a viscosity. Although a viscosity

free system is desirable at times, to achieve realistic dynamics we need to incorporate the effects of viscosity back into the interatomic forces. The following adjustments are made to Newton's laws of motion

$$m_i \frac{dv_i}{dt} = -\frac{\partial U(r^N)}{\partial r_i} + f_{friction}(v_i) \quad (2.13)$$

The force includes a frictional force due to the solvent.

$$f_{friction}(v_i) = -\gamma_i m_i v_i + R \quad (2.14)$$

where γ_i is the frictional coefficient and R is random force due to stochastic collisions with solvent particles. R is often defined from a Gaussian distribution with zero mean and variance that depends on the mass of the particles.

2.1.9 Green- Kubo Formalism For Viscosity

P_{xy} is related to velocity gradient by Eq 2.15.

$$P_{xy} = -\eta \frac{\partial v_x}{\partial y} = -\lim_{t \rightarrow \infty} \frac{\langle p_{xy}(t) \rangle}{\gamma} \quad (2.15)$$

where γ is the shear rate and P_{xy} is the non-equilibrium average of the pressure tensor and η is the shear viscosity. So, the shear viscosity expression when mathematically simplified comes down to Eq 2.16.

$$\eta = \frac{V}{k_B T} \int_0^\infty dt \langle p_{xy}(0) p_{xy}(t) \rangle \quad (2.16)$$

The shear viscosity is thus a function of the time correlated function of the pressure tensor. Eq 2.16 is used for the viscosity calculations in all the MD simulations.

2.1.10 Radial Distribution Function

In statistical mechanics radial distribution function or pair correlation in a system of particles gives an idea of the density of molecules in the box as a function of distance from a reference particle. Simply, it can be described as the probability of finding a particle at a distance r from the reference particle. It is of fundamental importance as it can be used to link microscopic details to macroscopic properties. It also gives an idea of the approximate size of the box. The representation of a typical RDF curve is given in figure 2.3.

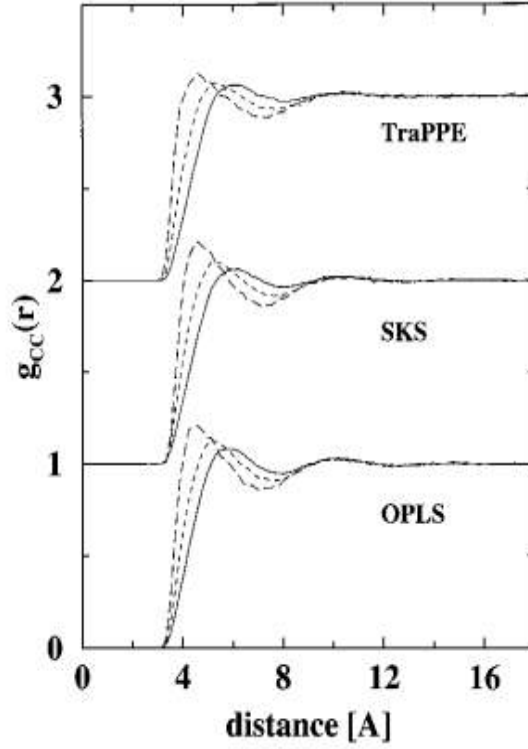


Figure 2.3: Intermolecular site radial distribution function of n-octanes as observed by Chen et al. [11].

2.2 MONTE CARLO SIMULATIONS

Gubbins et al[18] used on a conventional canonical MC system of 500 atoms. The cut-off was varied but in all cases r_c was greater than 4.0σ and the specific cut-off is also listed. The system was equilibrated for 2.5×10^6 configurations and was averaged for another 1.5×10^7 configurations. The maximum displacement was adjusted during the simulation and acceptance ratio was set to 40%.

Chen et al. [27] treated CH_x as the pseudo atom in TraPPE (transferrable potentials for phase equilibria) located at the sites of the carbon atoms and all other atoms (hydroxyl O and H) are modelled explicitly. Because of the partial charges between O and H of the alcohol the LJ potential was tweaked to describe a more rounded non-bonded interaction which included Coulombic interactions.

$$U_{coul} = \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \quad (2.17)$$

where q_i and q_j are the partial charges for the i^{th} and j^{th} atom respectively.

Lorentz Berthelot [7][8] combining rules are used to evaluate σ and ϵ .

$$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2} \quad (2.18)$$

$$\epsilon_{ij} = (\epsilon_i \epsilon_j)^{\frac{1}{2}} \quad (2.19)$$

In TraPPE force field, $CH_x - O$, $O - H$ and $CH_x - CH_y$ bonds are all fixed. The harmonic bending potential as given in equation 2.20 was described by a quadratic Taylors' expansion of the bond angle deviation [9] and the torsion potential as given in equation 2.21 was described by a third order cosine function [28].

$$U_b = \frac{1}{2} k_b (\theta_i - \theta_0)^2 \quad (2.20)$$

$$U_t = c_1(1 + \cos \phi_i) + c_2(1 + 2 \cos \phi_i) + c_3(1 + 3 \cos \phi_i) \quad (2.21)$$

Monte Carlo was executed for systems by Chen et al (sizes in brackets): methanol (500), ethanol (300), propan-1-ol (200), propan-2-ol (200), butan-2-ol (240), 2-methylpropan-2-ol (200), pentan-1-ol (150), pentan-1,5-diol (150) and octan-1-ol (120)[27]. The combined volume was adjusted to yield linear dimension of 30 Å and contain about 10 molecules in vapour phase. The cut-off radius used for truncation of potential was set at 14Å. System was equilibrated for 10000 steps and averaged for another 50000 steps. Moves like translational, rotational, conformational, volume exchanges and particle swaps were adjusted as to accommodate one volume exchange or particle swap per 10 MC cycles. Standard deviation of the ensemble averages is computed by averaging over five blocks .

The MC simulation for alkanes was carried out for a system capacity ranging from 200 for n-dodecane to 400 molecules for methane. Simulations were equilibrated for 5000 cycles and the production period was 5000 to 10000 cycles (OPLS or SKS) and 25000 (TraPPE) MC cycles[29]. The LJ potential, bond bending potential and torsion potential are given by equation 2.17, 2.20 and 2.21 respectively. Also, Lorentz Berthelot combining rules given by equation 2.18 and 2.19 are used to calculate the length and energy parameters. Maggs et al.[30] performed MC simulation for TIP3p model for water was created using Langevin thermostat, friction $1ps^{-1}$, integration step 1fs. A cube of 18.62 Å was used and 203 sites of water is used. Acceptance rate was tuned to 40 %. NVT simulations were performed at 300K.

Boulougouris et al.[31] carried out MC simulation of pure water in two boxes simultaneously using Gibbs ensemble. Three moves are used (ratio in brackets): particle displacement (84.5%), volume fluctuation (0.5%) and particle interchange (15%). The total number of water molecules (200-250) is kept constant in the two boxes. A run

consists of $(4 - 6) \times 10^6$ moves for equilibration in the temperature range of 300-400 K and $(1 - 1.5) \times 10^6$ moves at higher temperatures. The properties are averaged over $(3 - 4) \times 10^6$ moves in all cases. Initial configurations are either fcc or based on final configurations from previous runs carried out under similar conditions. Erpenbeck[32] used Monte Carlo simulation to find the viscosity using Green Kubo relations near the triple point of the LJ fluid. The viscosity coefficients are found to agree with the results of earlier papers in the same temperature region. The pressure is found to be independent of the number of molecules in the system but the viscosity appeared to be linear to the inverse of the number of molecules.

2.3 MOLECULAR DYNAMICS

Aneesur Rahman[4] did the first ever molecular dynamics simulation. He simulated a box of 216 rigid water molecules at a temperature of 34.3°C. He found good agreement with the results of experimental data.

Berk Hess[33] has devised a different number of methods to calculate viscosity like pressure fluctuations, momentum fluctuations and periodic fluctuations and has applied these methods to Lennard Jones fluid and two water models.

Another research conducted by Lee[34] concentrated on the shear viscosity of pure water in SPC/E model using MD simulations over a temperature range of 300-550 K.

Song Lee[35] has also carried out MD simulations for n-alkane ($C_{12} - C_{80}$) at high temperatures nearer to 2300 K to calculate viscosity and diffusion constant. They observed abnormalities in the density and friction constant of long chains of n-alkanes at high temperatures.

Nevins et al[36]. have studied the viscosity calculations of NaCl solution and found a good compromise between run length and viscosity calculation.

Nuevo et al[37] have studied the temperature dependence of the self-diffusion coefficients and Mori coefficients of LJ fluids by MD simulation for a temperature range of 0.71-4.45 in reduced units. A system of 256 atoms has been considered and the time average for the mean squared displacement was taken for 500 time steps while the simulation was run for 200000 steps.

Matar et al[38]. have researched the self-diffusion coefficients of LJ fluids at different

pressures. Einstein method was used to find the diffusion coefficients. They have used temperature dependent interaction parameters and have successfully reduced the error by 67%. They have studied systems of 500, 1000 and 2000 atoms at a pressure of 13 bar and a temperature range of 90-135 K in isothermal, isobaric and NPT ensemble. The effect of time steps (2, 4, 6 and 8 fs) was also investigated.

Dysthe et al.[39] have performed NVT simulations using a Nose-Hoover thermostat. The total trajectory considered for calculation was 5ns with a time step of 5fs. They estimated viscosity at a precision of $\pm 10\%$. They also compared viscosity for two, three and seven component system. The number of time steps reduced with larger systems.

Allen and Rowley[40] studied systems representing a bunch of branched and linear alkanes. Their simulations started from linear alkane butane onwards to study the effect of chain length. Branched alkanes such as 2-methyl propane, 2,2-dimethylbutane and 2,2-dimethylpropane were studied to determine the model precision. They used transferrable potentials for alkanes known as OPLS. All simulations used 216 molecules and the cut-off radius was set up at 2.8σ . Time steps of 2.6-2.9 fs were used for each simulation. Before calculating the properties, however, the systems were equilibrated for 40 to 200 ps. They observed reasonable agreement with the results of Jorgensen et al.[6] for n-butane and cyclopentane only. Also, the density results agree with those of experimental value only at low densities.

Vrabec et al.[41] did a simulation study of a box size of 500 and 864 LJ molecules at a reduced time step of 0.001 for 100000 to 200000 time steps depending on the state point. The cut-off radius was fixed at 5σ for small volume and half the box length for others. NVE ensemble was used to average the transport coefficients after equilibration is reached. They found good agreement with the experimental results of argon, krypton, xenon and methane. Lower deviations are observed at low densities and the deviation increases to 15 % for xenon and 20% for methane.

Boned et al. [29] have presented a correlation of viscosity of LJ fluid for a wide range of temperatures. They have even proposed a corresponding state that fits nicely in conditions that cover gas, liquid and supercritical state. They have also obtained the viscosity results for multi-component mixture using one fluid van der Waals approximation but the results deviate when they take an asymmetric mixture.

Edberg et al[42] have performed shear simulation on n-butane and n-decane and have observed non-linear responses. They have extrapolated the values of zero shear viscosities and the results agree nicely with experimental data. They have run the butane simulations

for 64 molecules truncated at 2.5σ and the decane simulations for 27 and 54 molecules. They have used a time step of $1.92 \times 10^{-15} s$ and the simulation run lengths range from 270ps for butane to 1100 ps for decane.

Nicholas et al[43] studied the effects of diffusion of methane and propane in silicates and have found excellent agreement with NMR results. They have simulated methane at infinite dilution and density of 2, 4, 8, 12 and 16 molecules per unit cell. They have also simulated propane at infinite dilution and a loading of 4 and 12 molecules per unit cell to study its bulk properties.

Ryckaert et al.[44] have studied the shear viscosity of butane using Green-Kubo formalism and a non-equilibrium method. They observed that the tail correction did not affect the viscosity coefficient. They found that both the methods produced results that agreed well with each other.

Daivis and Evans [45] used Ryckaert-Bellemans[44] model of n-butane to predict diffusion coefficient, linear viscosity and thermal conductivity. They used system sizes of 64 and 864; however, they did not observe that the dependence of viscosity and thermal conductivity on system size is negligible. They also found that the self-diffusion coefficient increases with system size.

Tseng et al[46] observed the shear thinning and shear dilatancy of n-hexadecane to study pressure temperature and density effects. They observed that at low shear rates (less than $10^{11} s^{-1}$), the properties of the fluid showed that it was near Newtonian regime. However, at greater stress the fluid shows shear dilatancy.

Chapter 3

Results and Discussion

The average energy and average pressure of LJ fluid at different reduced temperature and reduced pressure was predicted using Monte Carlo simulation. MC was used to study the average density of water, alcohols (ethanol and propan-1-ol) and alkanes (methane, propane and butane). The results were compared with experimental data.

Molecular Dynamics Simulation was used to predict the average energy and viscosity of LJ fluid at different temperatures and box density. MD was also used to predict the viscosity of alkanes (ethane, propane, butane and isobutane) at different temperature. The cut off radius was also varied to study the effect of variation of box size on the predicted viscosity. MD was used to simulate the viscosity of mixture of ethane and propane at different temperature and at different box sizes.

3.1 SIMULATION DETAILS

The MC simulation code for LJ fluid was written in MATLAB. The system is an NPT ensemble of 500 particles. The simulation was run at constant density with increasing temperatures and then with increasing density at constant temperature. The entire simulation was equilibrated for 15000 cycles and then averaged over 25000 cycles. Reduced density (Eq. 2.4) is varied in the range of 0.1-0.9 and reduced temperature (Eq. 2.5) is varied in the range of 1-2 which is the typical simulation temperature.

MC simulation for finding the average density of alkane (methane(500), propane(200) and butane (300)) was carried out at various temperatures and the average density and average energy are calculated. Numbers in curly brackets indicate the number of molecules taken in simulation run. Similarly 200 molecules for both the methanol and propan-1-ol systems and 320 molecules of water are taken in the MC simulation study. Three models of water are simulated namely SPCE, TIP3p and TIP4p. The parameters for all the models are taken from Lee et al. and Maggs et al. [30], [34]. RDF (Radius distribution frequency) curves were used to determine an appropriate cut off radius for the systems.

WATER MODELS: SPCE, TIP3p and TIP4p

There are mainly three types of water models: rigid, flexible and polarizable model. The structures are named depending on the number of interaction sites which are mainly 3-5. SPC and TIP3p are both three-sites model. The partial positive charge on the two hydrogen atoms evenly balances out the negative charge on the oxygen. The model uses LJ potential to calculate interaction between two molecules with the interaction point centered at the oxygen for each individual molecule. The van der Waals force between hydrogen is neglected. The only difference between both is the charge distribution and the other parameters as noted in Table 3.1. The SPC/E model uses an additional polarization correction to the potential energy function. The TIP4p model transfers the negative charge along the bisector of the H-O-H angle. The various parameters for TIP4p are recorded in table 3.2.

In the present study MC simulation was performed to predict the average density of water by using SPCE, TIP3p and TIP4p models.

Table 3.1: Parameters for TIP3p, SPC and SPC/E model

Parameters	TIP3p	SPC	SPC/E
$r(\text{OH}), \text{\AA}$	0.9572	1.0	1.0
HOH, deg	104.52	109.47	109.47
A $10^{-3} \text{kcal} \text{\AA}^{12} / \text{mol}$	582	629.4	629.4
$q(\text{O})$	-0.834	-0.82	-0.8476
$q(\text{H})$	0.417	0.41	0.4238

Table 3.2: Parameters for TIP4p model

$r(\text{OH}), \text{\AA}$	0.9572	$q(\text{O}) (e)$	0
HOH, deg	104.52	$q(\text{H}) (e)$	0.52
$\sigma, \text{\AA}$	3.154	$q(\text{M}) (e)$	-2 $q(\text{H})$
$\epsilon/k_B, \text{K}$	78.0	$r(\text{OM}), \text{\AA}$	0.15

The MD simulation to find average pressure and average energy for argon was carried out in a NVT ensemble for 500 molecules. In the simulation study, the reduced density was varied in the range 0.05 to 1.2 and reduced temperature from 1.3 to 6.0. The entire simulation was run for 1000 steps. The MD simulation for argon in LAMMPS to predict its viscosity was done for reduced density ranging from 0.1 to 1.0. The simulation was

performed at 4 reduced temperatures: 1, 2, 3 and 4.

The MD simulation for alkane (ethane, propane, butane and isobutene) was first carried out in an NVE ensemble for 10,000 steps to initialize the motion. The equilibration was done in an NPH ensemble or a Langevin thermostat was employed to maintain the temperature in the range of the boiling points of the individual alkane for a time span of 20fs. Then the equilibrated system was subjected to an NPT ensemble to stabilise the pressure and a Berendsen thermostat was added to ensure and maintain the temperature and pressure for another 1, 00, 000 time-steps. System size varied over 18 to 512 atoms to examine the effect of system size. Cut-off was varied to examine its effect on viscosity. Simulation details are shown in Table 3.3.

Table 3.3: Various simulation details for MD simulation of alkane

MOLECULE	SYSTEM SIZE (no. of molecules)	TEMPERATURE, K
Ethane	48	80-240
Propane	36, 64, 128, 256, 512	100-300
Butane	36, 125, 216, 512	100-350
Isobutane	36, 64, 128, 256, 512	160-350
1:1 Mixture of Ethane and Propane	64, 128, 256, 512, 1000	160-250

MD simulation was performed for a mixture of ethane and propane with system size varying from 36 to 1000 molecules in a 1:1 ratio to determine the effect of system size on viscosity. Cut-off was also varied here to examine its effect on viscosity. Green-Kubo methods[32] were employed to find out the average viscosity for each simulation. Simulations are carried out in LAMMPS, an open source environment, on an Intel® Core™ i5 CPU processor.

3.2 RADIAL DISTRIBUTION FUNCTION

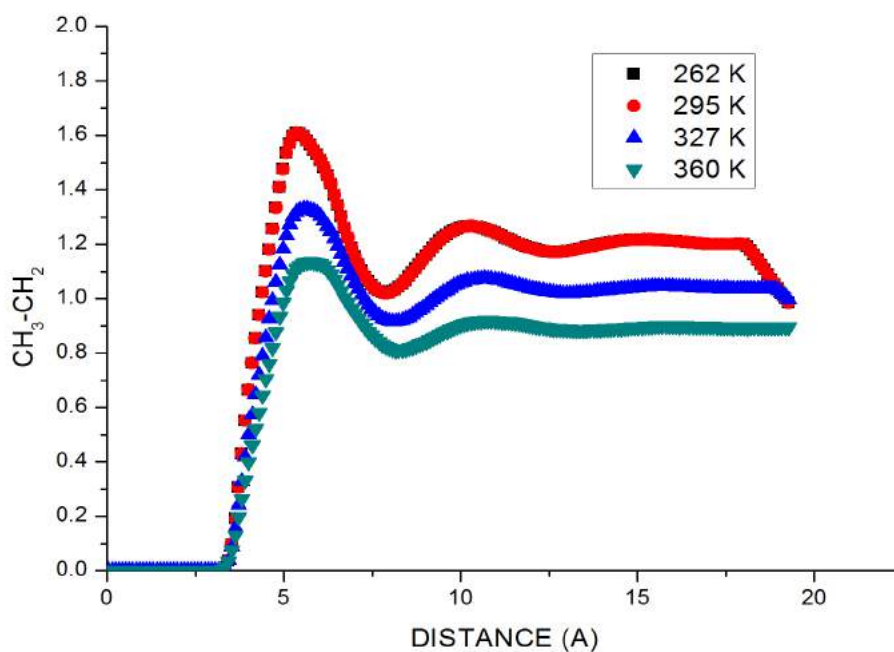
Radius distribution function is obtained between two molecules inside the box. It can also consider a group of atoms as a molecule and find RDF between such groups. It is defined as the probability of finding the latter molecule at imaginary spheres of definite distance considering the earlier molecule as the centre of the sphere.

RDF distribution curves were used to find a suitable cut-off radius. The cut-off radius

is the radius at which the RDF curve saturates or the limiting distance after which all intermolecular attraction and repulsion forces can be safely neglected. The values of it as found from the RDF curves are tabulated in table rdf table. The cut-off radius from RDF helps to decide upon the starting value of cut-off radius for both MC and MD simulation. RDF for the simulated systems of alkane, alcohol and water are shown in figure 3.1-3.10.

Table 3.4: Molecular size and cut-off radius by RDF curves

MOLECULE (no. of molecules)	Cut-off radius, Å
Water(320)	16.0-18.0
Propanol (200)	10.0-12.0
Ethanol (200)	12.0-14.0
Propane (200)	12.0-14.0
Butane (300)	15.0-18.0

Figure 3.1: RDF of $CH_3 - CH_2$ pair of butane at different temperatures

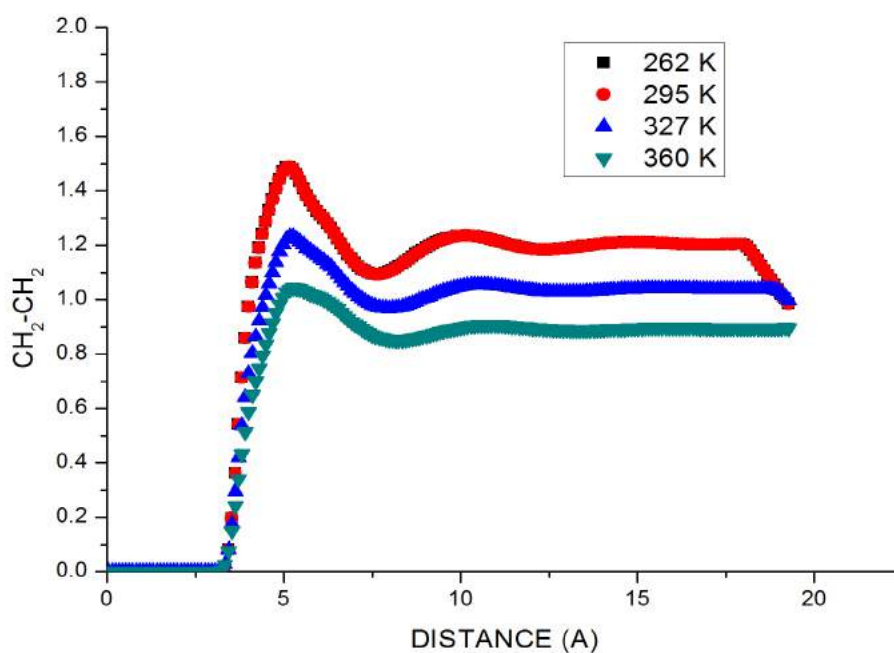


Figure 3.2: RDF of $CH_2 - CH_2$ pair of butane at different temperatures

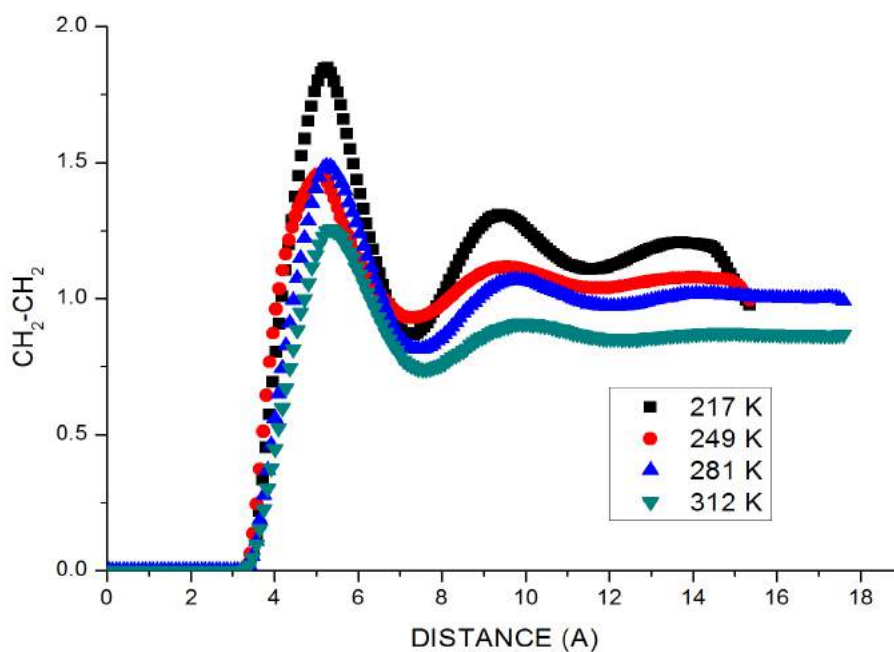


Figure 3.3: RDF of $CH_2 - CH_2$ pair of propane at different temperatures

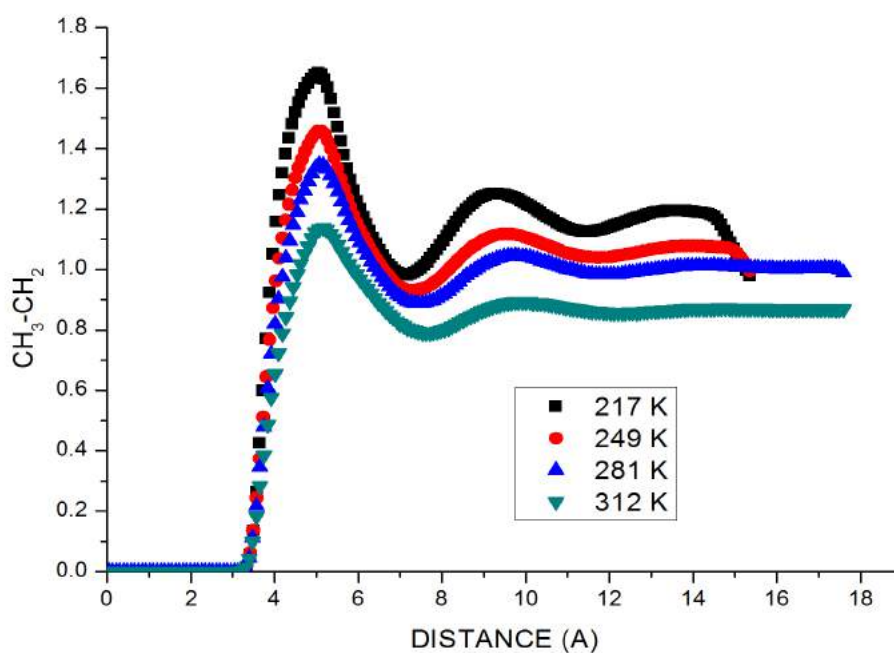


Figure 3.4: RDF of $\text{CH}_3 - \text{CH}_2$ pair of propane at different temperatures

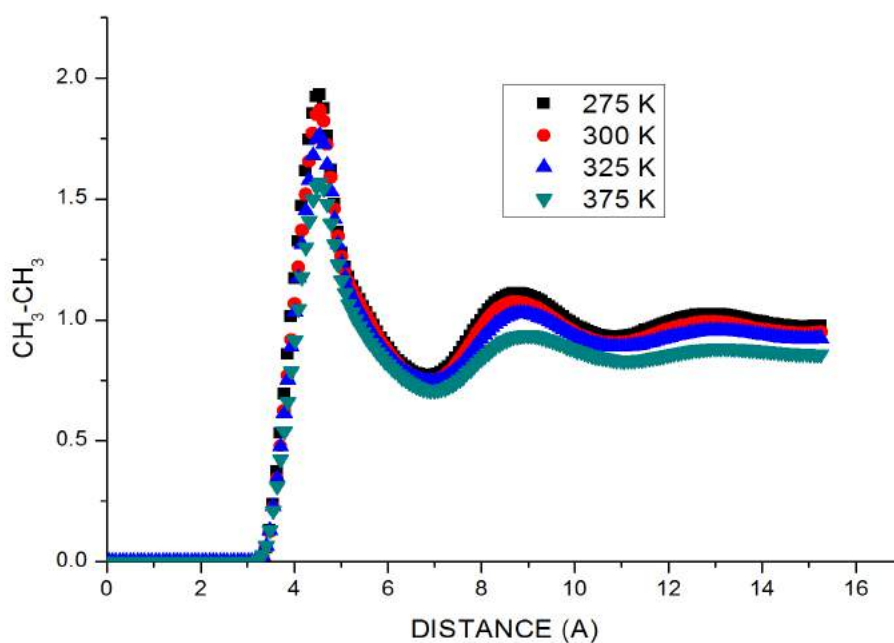


Figure 3.5: RDF of $\text{CH}_2 - \text{CH}_2$ pair of ethanol at different temperatures

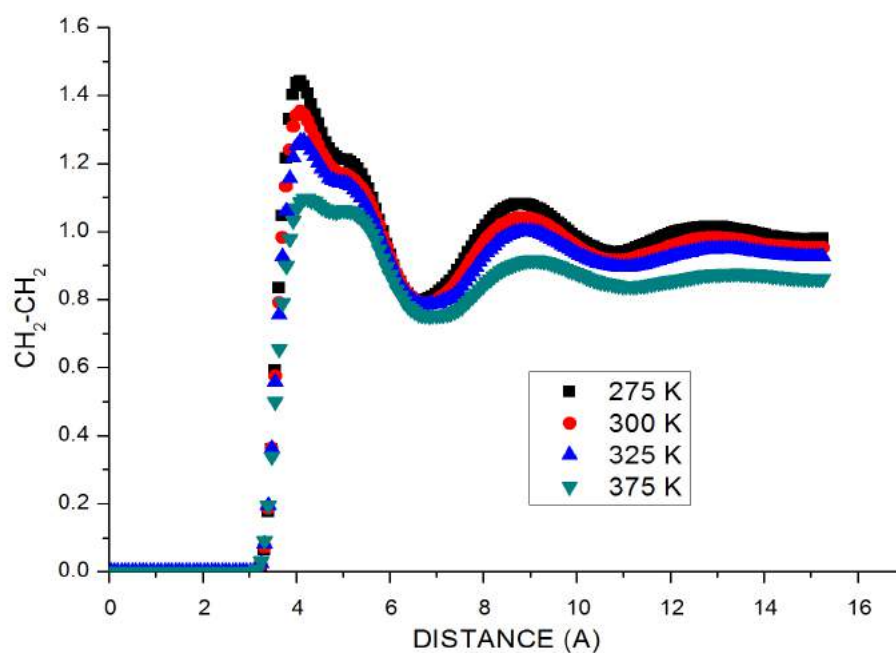


Figure 3.6: RDF of $\text{CH}_3 - \text{CH}_2$ pair of ethanol at different temperatures

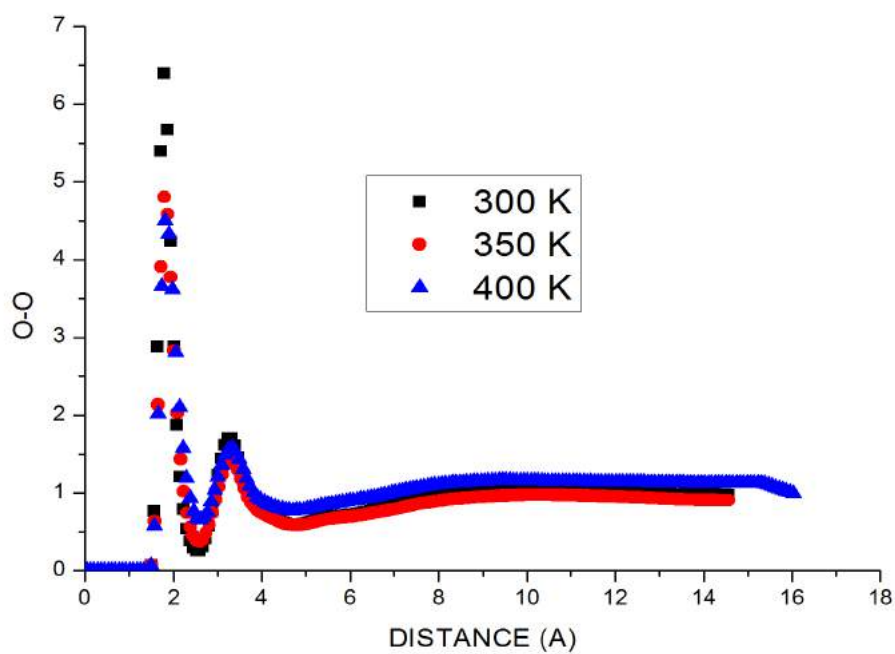


Figure 3.7: RDF of $\text{O} - \text{H}$ pair of propanol at different temperatures

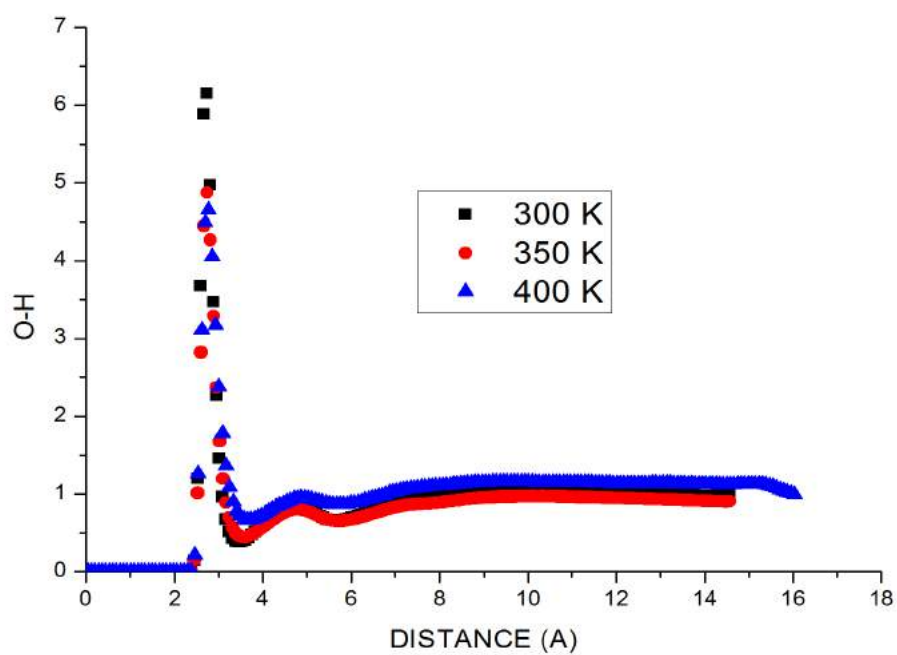


Figure 3.8: RDF of $O - O$ pair of propanol at different temperatures

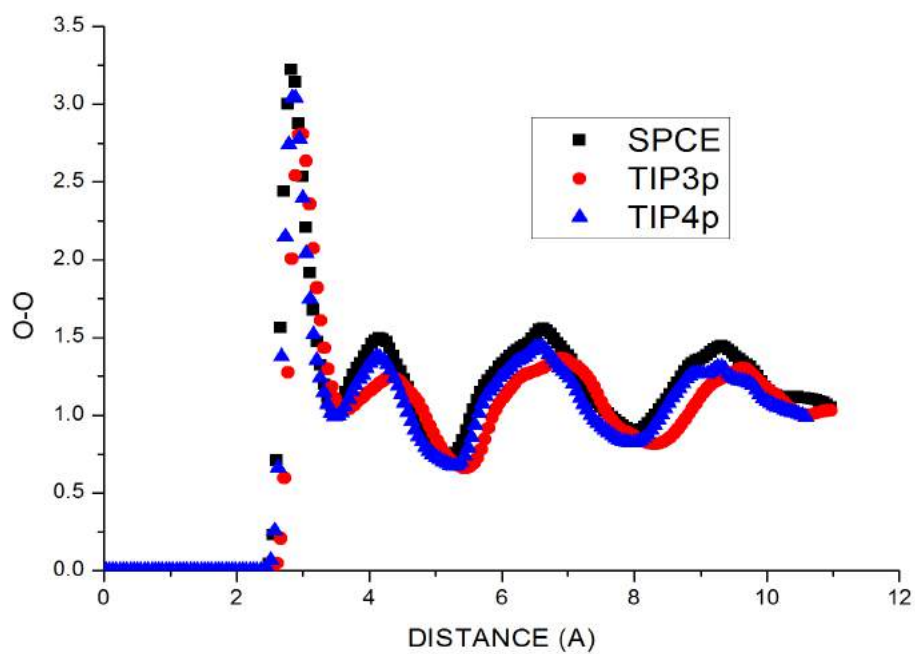


Figure 3.9: RDF of $O - O$ pair of water at different temperatures

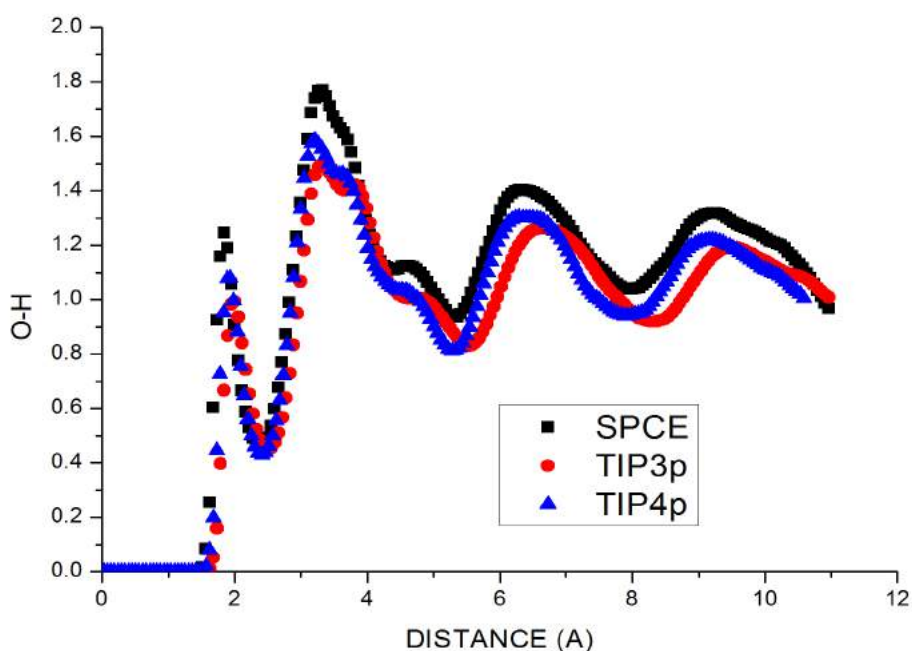


Figure 3.10: RDF of $O - H$ pair of water at different temperatures

3.3 ESTIMATION OF PROPERTIES BY MC SIMULATION

The MC simulated results of average energy for argon obtained in the present study are compared with the results of Gubbins et al[18]. The graphical comparison of average energy computed from MC simulation with Gubbins et al [1] is shown in figure 3.11. The standard deviation computed was found to be 0.5022.

The predicted energy becomes less accurate at higher density. At higher densities, the molecules interact at distances that are outside of the cut-off boundaries. Thus, a significant number of such interactions are neglected. This leads to erroneous results at high densities. One way to reduce such error is to increase the cut-off boundary. But, this leads to a very high computational time. Another way is to increase accuracy of the prediction by increasing the number of molecules in the box. This would minimise the pressure fluctuations and would give better results. But this also involves with the large increase in the computational time.

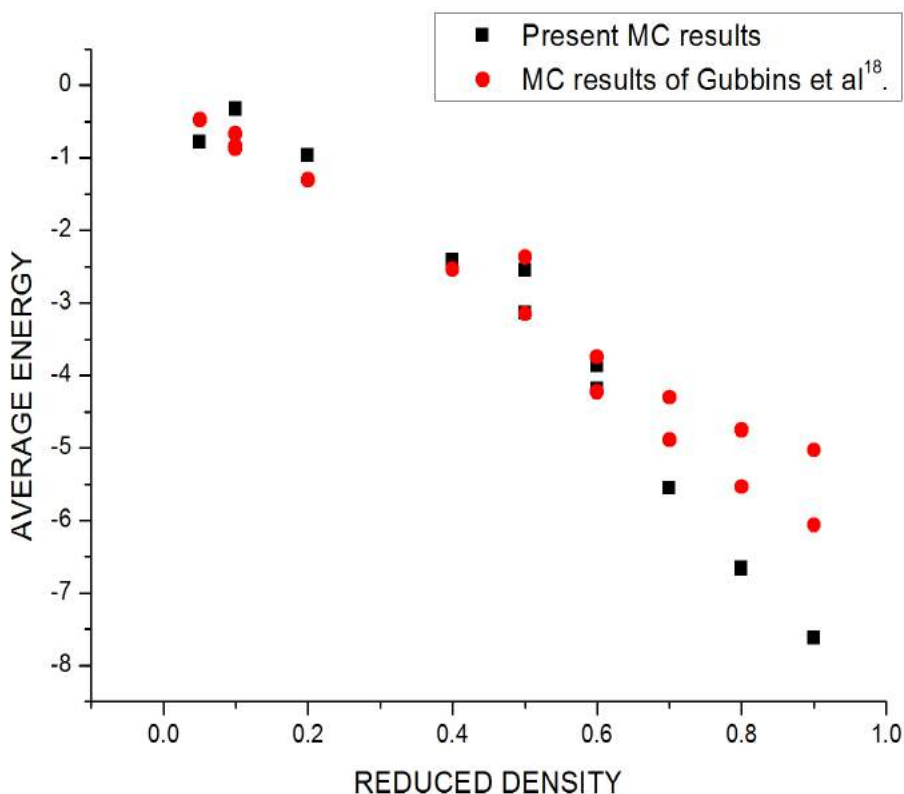


Figure 3.11: Comparison of average reduced energy of LJ fluid as found from MC simulation in present study with that of Gubbins et al. [18].

The MC simulation to find the average density of alkane (methane, propane and butane) at different temperatures was carried out, and the results are compared with Martin et al.[9] in figure 3.12. In the same figure, the MC simulated average density of alcohol (methanol and propan-1-ol) are compared with the results from Chen et al [27]. It shows a satisfactory prediction of properties of both alkane and alcohols by the present MC simulation study. The standard deviation for alkane and alcohol was observed to be 0.0232 and 0.0273 respectively. The results are tabulated in Table 3.5. In figure 3.13, the average density of water as predicted from the three models is compared with the experimental value of 1.0 g/cm³. The mean square error was found to be 0.015.

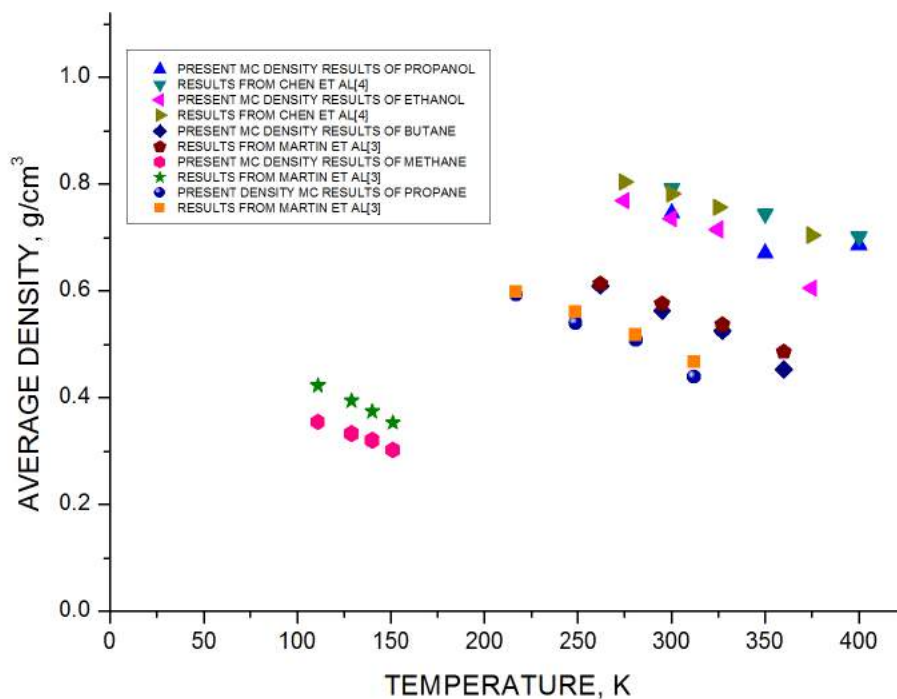


Figure 3.12: Comparison of average density of methane, propane, butane, ethanol and propan-1-ol as found from MC simulation in present study with that of Martin et al [9] and Chen et al [27].

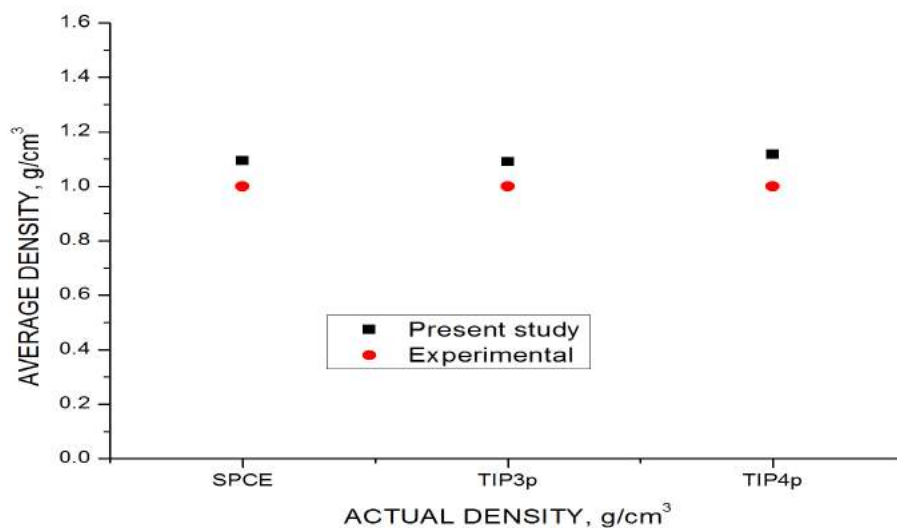


Figure 3.13: Comparison of average density of water as found by MC simulation in present study with experimental value

Table 3.5: MC simulated results of average density and average energy of water, alcohols and alkanes

	Temperature, K	Avg. density, g/cm^3	Exp. values	Error	Avg. Energy
Water					
SPCE		1.092	1	0.092	-10.13
TIP3p		1.088	1	0.088	-9.084
TIP4p		1.116	1	0.116	-9.114
Propanol					
	300	0.744	0.792	-0.047	-8.414
	350	0.671	0.744	-0.073	-7.503
	400	0.686	0.702	-0.016	-7.841
Ethanol					
	275	0.764	0.804	-0.036	-8.712
	300	0.735	0.782	-0.046	-8.395
	325	0.715	0.756	-0.041	-8.045
	375	0.605	0.705	-0.100	-7.101
Butane					
	262	0.610	0.613	-0.003	-4.036
	295	0.563	0.576	-0.013	-3.890
	327	0.525	0.536	-0.010	-3.586
	360	0.453	0.486	-0.033	-3.068
Methane					
	111	0.354	0.423	-0.068	-1.392
	129	0.333	0.394	-0.060	-1.327
	140	0.321	0.374	-0.053	-1.276
	151	0.303	0.353	-0.050	-1.220
Propane					
	217	0.593	0.598	-0.005	-7.219
	249	0.539	0.560	-0.021	-3.205
	281	0.508	0.517	-0.008	-3.039
	312	0.439	0.467	-0.027	-2.610

3.4 RESULTS OF MD SIMULATION

In MD simulation velocity of the molecule is used as input and the potential function includes both non- bonding energy (LJ potential) and bonding energy (bond stretching, bond bending and dihedral forces) which were neglected in MC calculation. In turn, MD simulation takes lesser computational time than MC simulation for the same size of system. Hence, MD simulation was performed for the same LJ fluid with same density and temperature as used in the MC simulation. The error in the predicted energy and pressure was found to be very less, sometimes of the order of 1% for MD simulation. The comparison of average pressure and average energy estimated from MD simulations with Gubbins et al[18] is depicted in figure 3.14 and 3.15 respectively. The results of present study was found to deviate by 14.96% when compared to Gubbins et al[18].

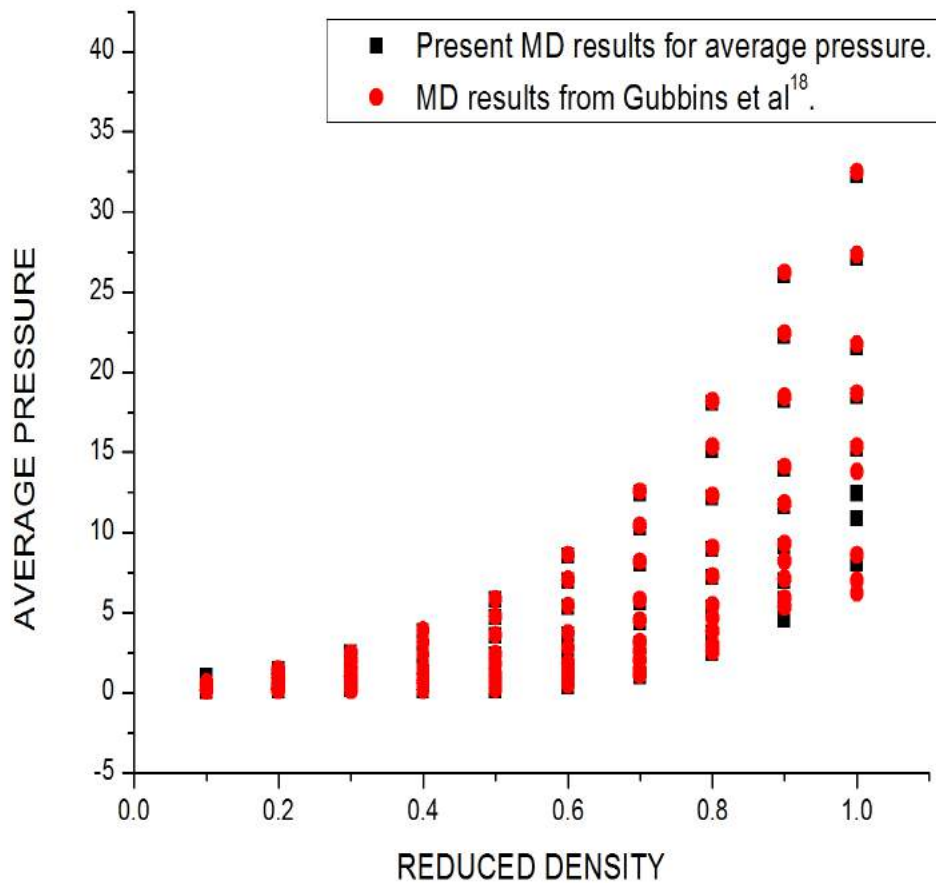


Figure 3.14: Comparison of average reduced pressure of LJ fluid as found from MD simulation in present study with that of Gubbins et al [18].

The results of MD simulations are very close to the results of Gubbins et al[18]. So, MD simulation is more accurate to model real fluids than MC simulation and also helps to save valuable computational time.

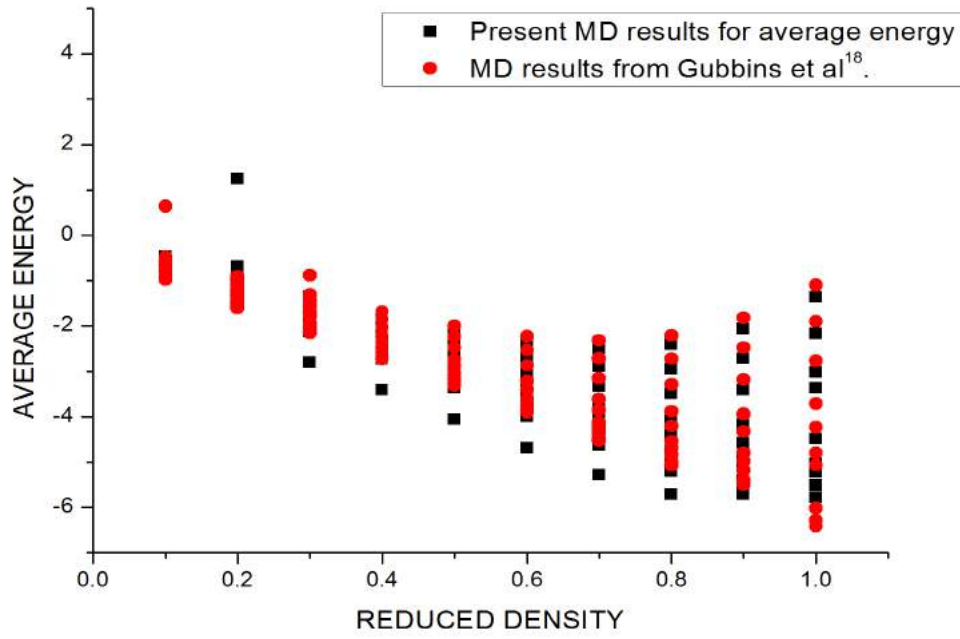


Figure 3.15: Comparison of average reduced energy of LJ fluid as found from MD simulation in present study with that of Gubbins et al. [18].

The viscosity of LJ fluid was also calculated with MD simulation in LAMMPS. The results are shown in figure 3.16. The viscosity was found to be increasing with increasing density and increasing temperatures. The standard deviation compared with Boned et al[29] was observed to be 0.159033.

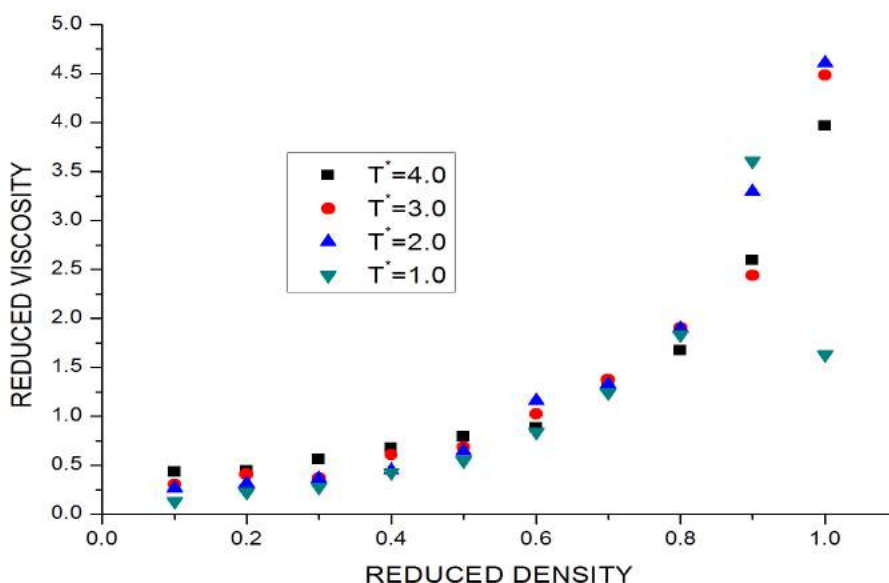


Figure 3.16: Reduced viscosity of LJ fluid at reduced densities and temperatures.

Figure 3.17 and 3.18 depict the variation of viscosity and density with temperature for butane using number of molecules as the parameter. With lesser number of molecules, the randomness is greater. Hence, the viscosity of the fluid increases. The difference in the values of viscosity between 216 and 512 molecules is found less than that of 36 and 125. This shows that the change of the viscosity at higher size of the system become less significant. However, the density varies insignificantly with number of molecules which shows that density is an intensive property. The figures also show a decreasing trend of the variation of the properties with temperature at higher size of the system. With increasing number of molecules, the variation of density with temperature shows an expected decreasing trend. The results are compared with that of Aspen HYSIS results for unit flow rate at same temperature and pressure condition. The deviation was found to be decreasing with the number of atoms.

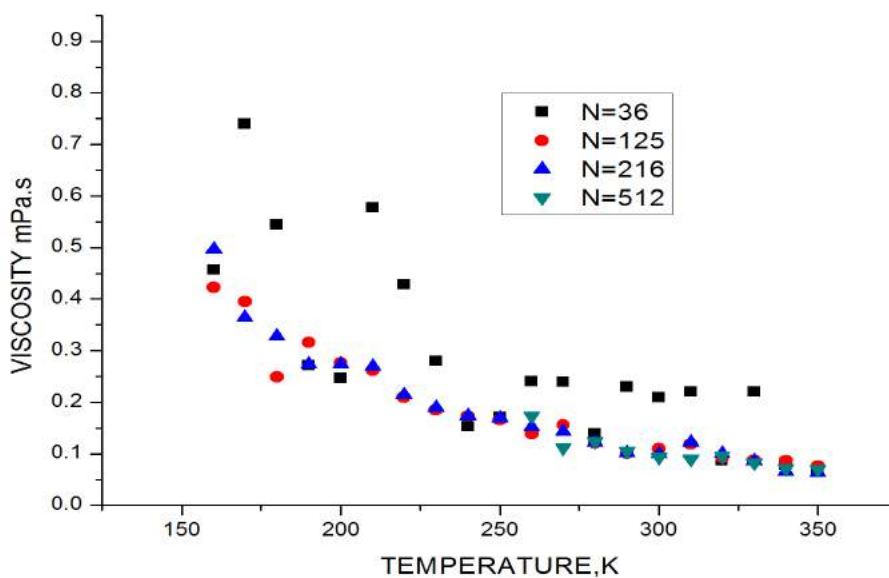


Figure 3.17: Variation of viscosity of butane with temperature.

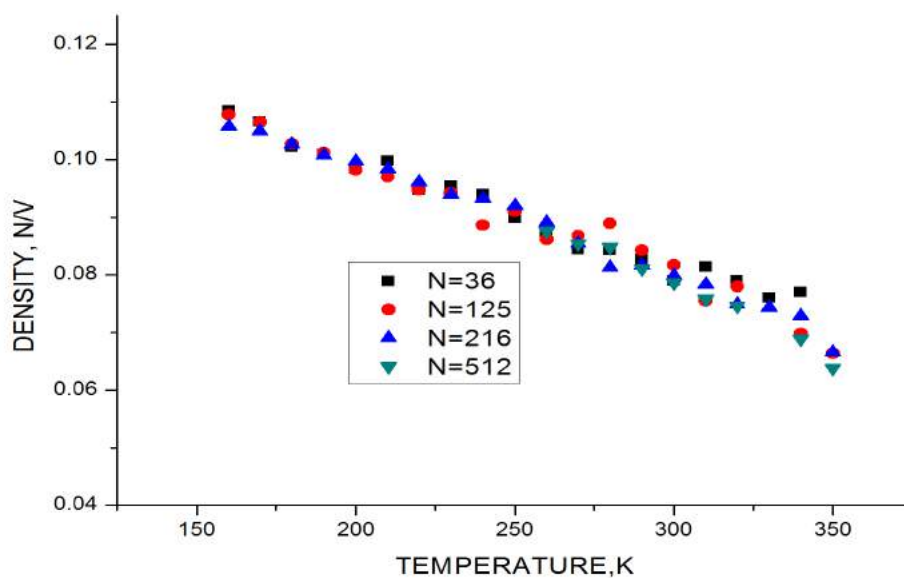


Figure 3.18: Variation of density of butane with temperature.

Figures 3.19 and 3.20 show the MD simulated results for viscosity and density of propane with temperature keeping number of molecules as the parameter. Both the curve shows similar trend as that of butane and can be explained in the similar way. The deviation was however found to be increasing with the number of atoms when compared with the viscosity of propane by HYSIS software. One reason could be the box is non-uniform

in size whereas the box was incremented uniformly for butane in all directions. But it is observed that when the molecules are replicated equally in all direction the deviation decreases. This is due to the assymetric expanse of butane in the three direction. Figures 3.21 and iso2 represent viscosity and density versus temperature for isobutane at different number of molecules. This also shows similar trend of decreasing viscosity with increasing number of molecules. The reason is same as that explained for butane. The density does not vary significantly with number of molecules which proves again that it is an intensive property. The deviation was measured from the results of HYSIS. It was again observed that the deviation increased with increasing number of molecules but the deviation decreased once the replication of molecules was similar in all direction. The deviation was found to be greater than that of butane. Branched molecules have different conformations which are not considered in the present study.

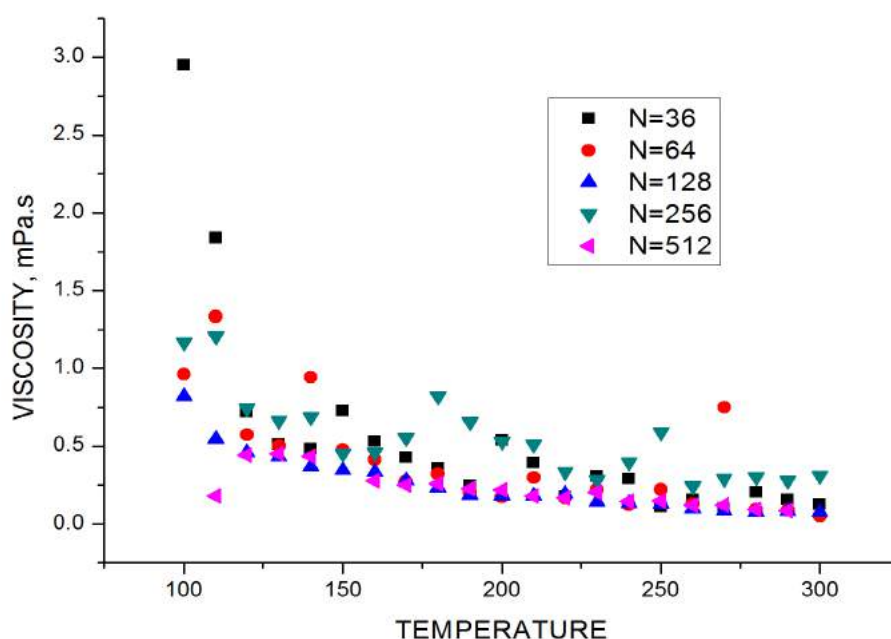


Figure 3.19: Variation of viscosity of propane with temperature.

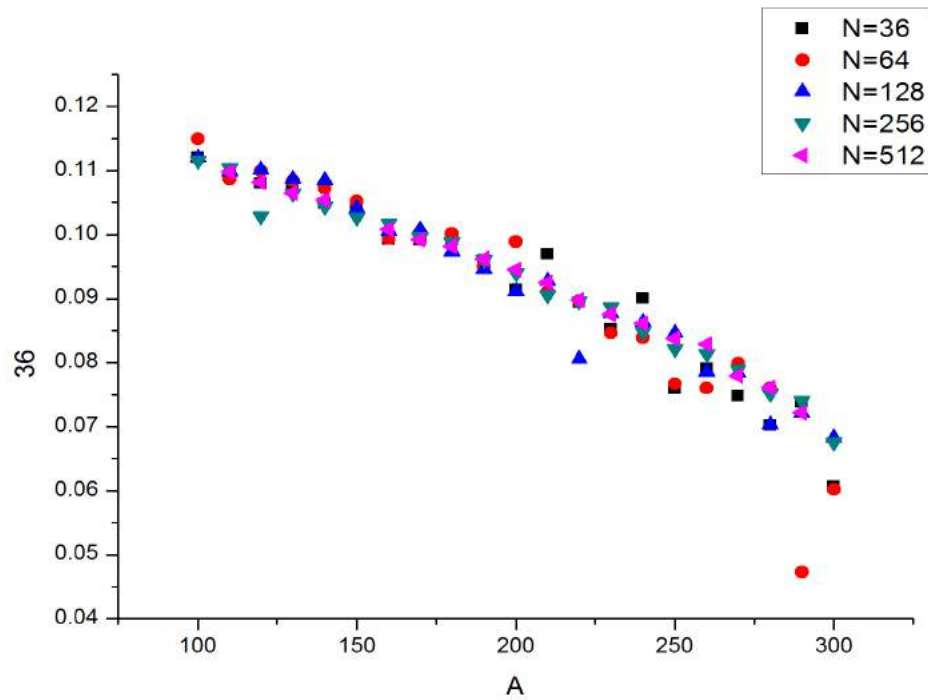


Figure 3.20: Variation of density of propane with temperature.

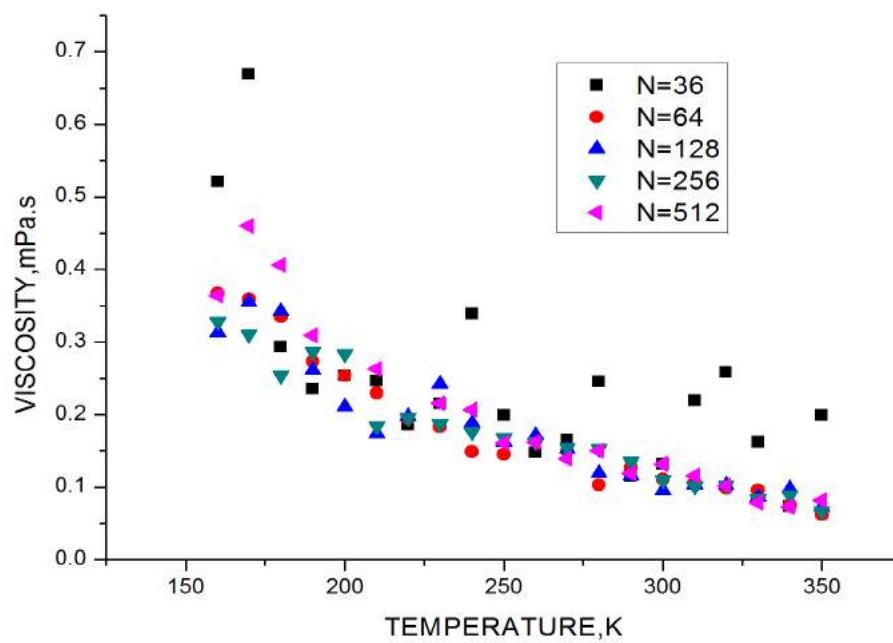


Figure 3.21: Variation of viscosity of isobutane with temperature.

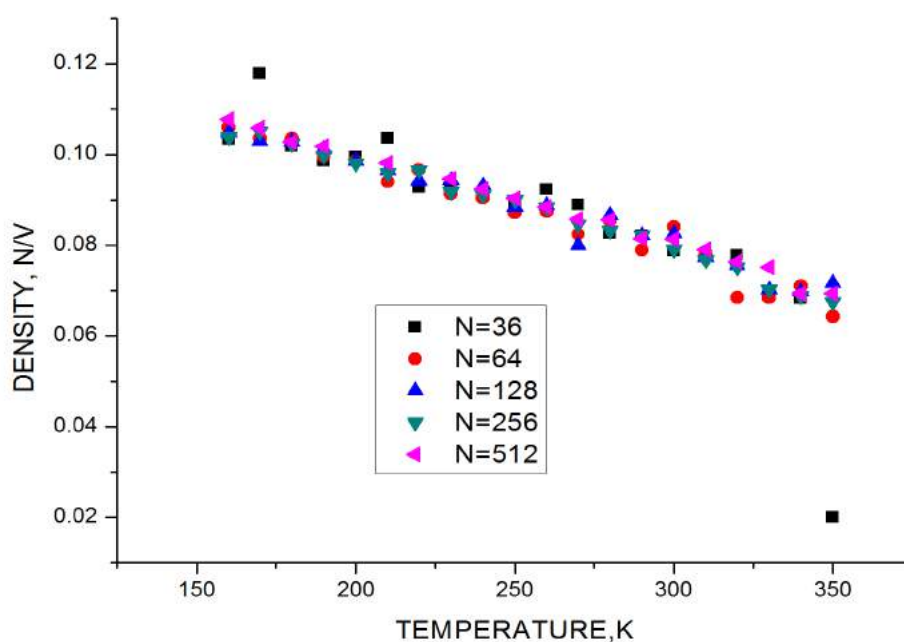


Figure 3.22: Variation of density of isobutane with temperature.

The simulation details for the prediction of viscosity of a mixture of ethane and propane in the ratio of 1:1 are tabulated in table 3.3. The results of viscosity and density versus temperature for the mixture are plotted in figure 3.23 and 3.24 respectively. The viscosity, as seen from the figure, is reduced with increasing number of molecules but found to increase with increase in cut-off. The decreasing trend with increasing number of molecules can be attributed to the reduced randomness of molecules at higher number density of the box. The increase in viscosity with increasing cut-off radius is due to more number of collisions that are taken into account while doing the simulations. The density remains same for the same number of molecules at different cut-off radius but increases with increase in number of molecules.

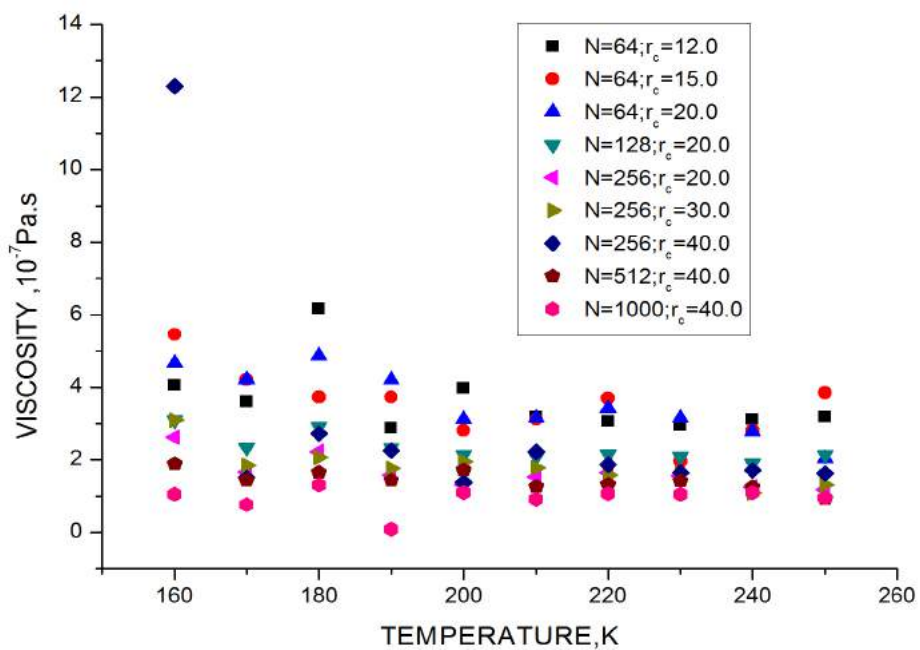


Figure 3.23: Variation of viscosity of (1:1) mixture of ethane and propane with temperature.

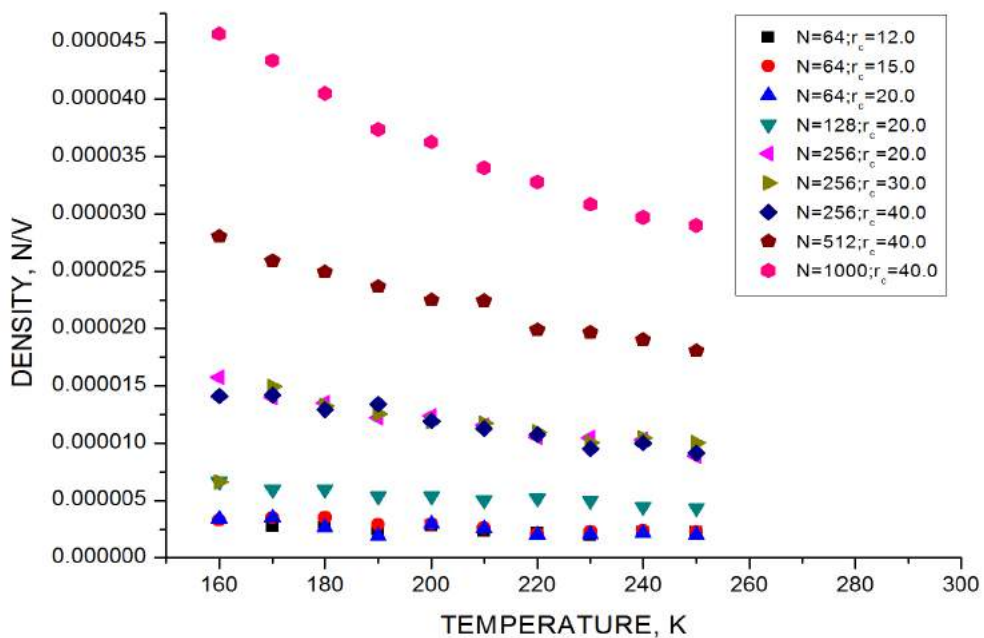


Figure 3.24: Variation of density of (1:1) mixture of ethane and propane with temperature.

For the mixture of ethane and propane, the effect of cut-off radius and box size on the viscosity and density are also studied. Density remains almost equal at all temperatures

thus establishing it is an intensive property. The viscosity and density of a box size of 256 molecules of ethane and propane in 1:1 ratio with cut off radius 20, 30 and 40 Å are plotted in figure 3.25 and 3.26 respectively. According to the figure, viscosity increases with increasing cut-off radius. As the cut-off radius increases more number of molecules participate in the calculation of intermolecular forces and hence, the number of collisions increases. This leads to higher viscosity at higher cut-off radius. The viscosity and density of box size of 256, 512 and 1000 molecules of mixture of ethane and propane in the ratio of 1:1 with a cut-off radius 40Å is plotted to study the effect of the box size on the properties. The distributions are shown in figure 3.27 and 3.28 respectively. The change of viscosity between two consecutive box sizes decreases with increasing box size. The simulating system behaviour tends to real system with increasing the box size. More number of atoms implies more surface molecules and that replicates a real system.

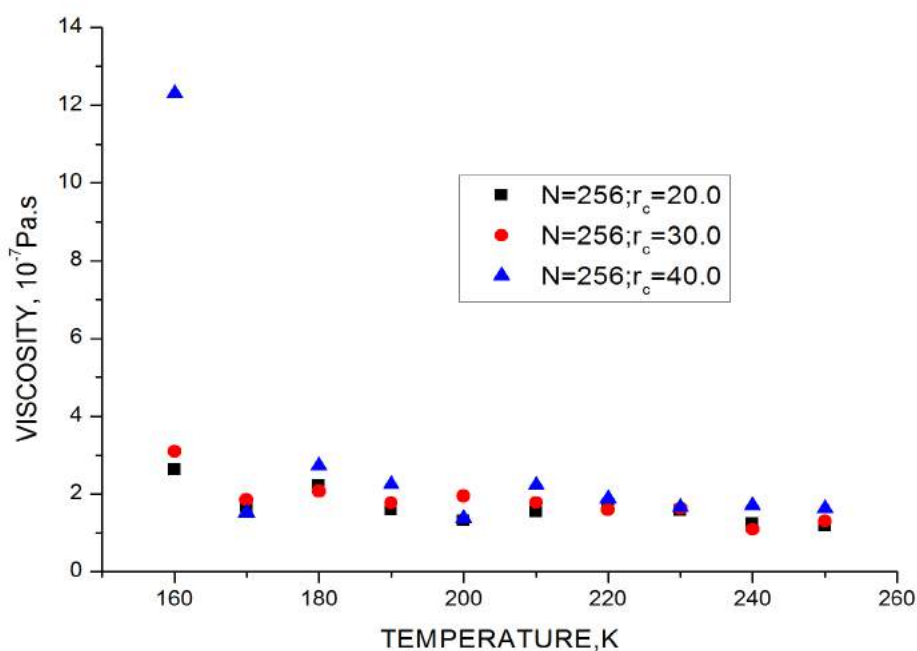


Figure 3.25: Variation of viscosity of (1:1) mixture of ethane and propane with temperature with 256 molecules in the box.

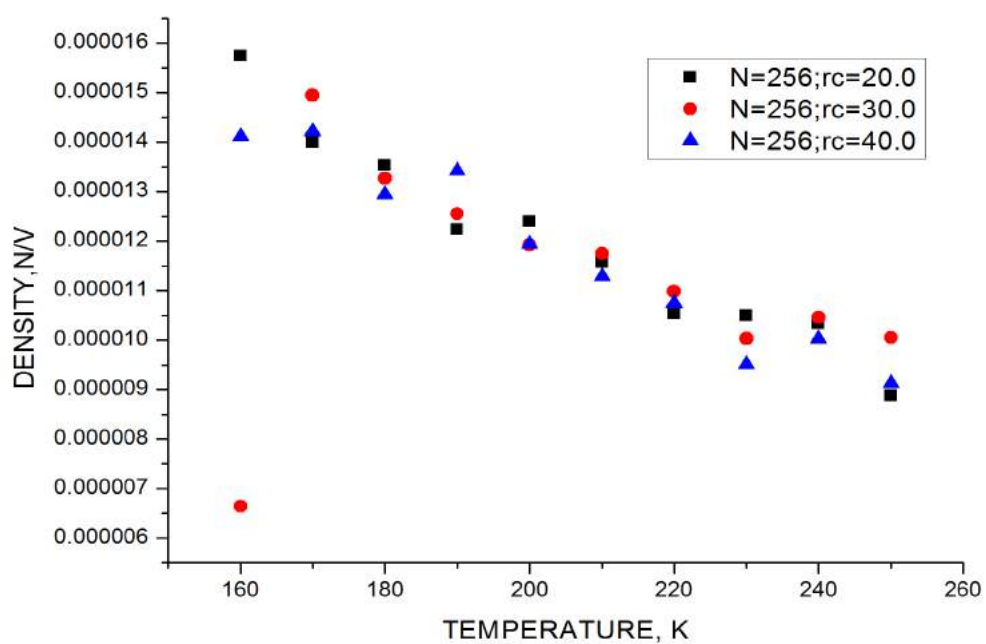


Figure 3.26: Variation of density of (1:1) mixture of ethane and propane with temperature with 256 molecules in the box.

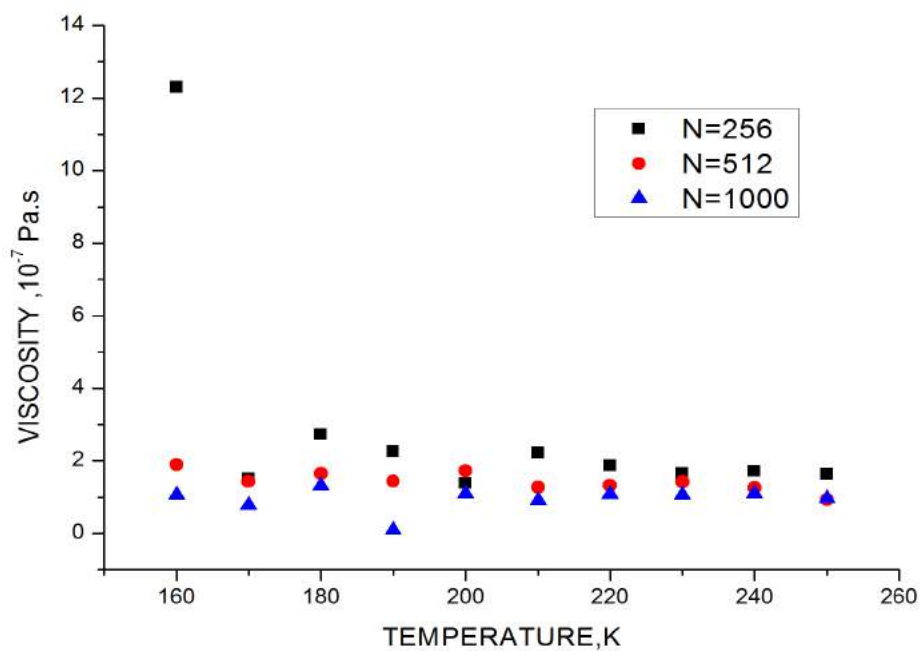


Figure 3.27: Variation of viscosity of (1:1) mixture of ethane and propane with temperature with cut-off radius, $r_c=40$ Å.

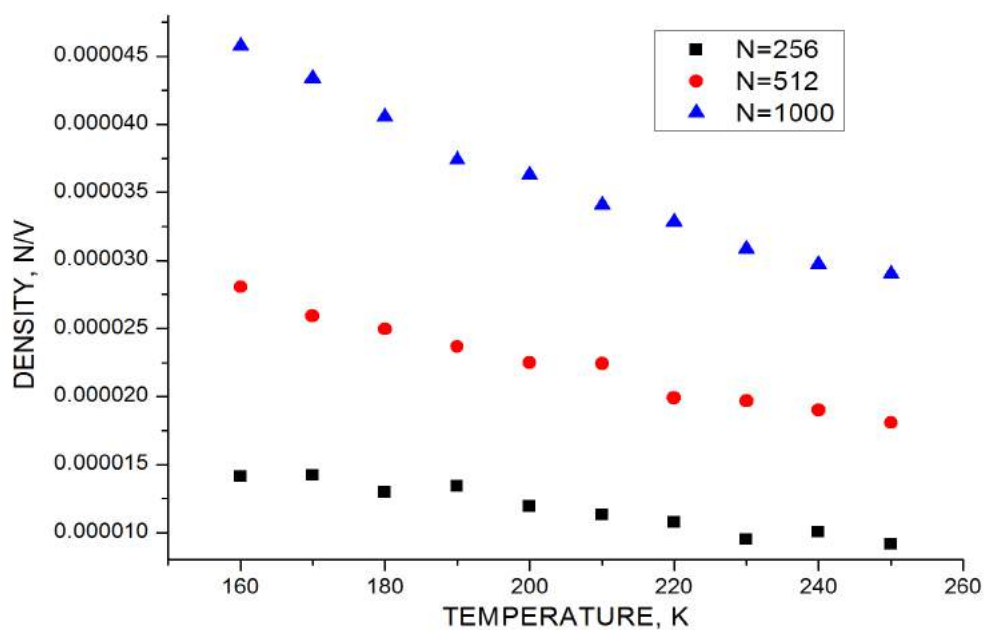


Figure 3.28: Variation of density of (1:1) mixture of ethane and propane with temperature with cut-off radius, $r_c = 40$ Å.

When the predicted density values of the ethane-propane mixture are compared with the predicted density values of pure propane it is observed that there was a difference in the order of magnitude of 10^4 . It was concluded that the molecules are in a gaseous phase. This was confirmed when the predicted density was compared with the vapour density results for the mixture obtained from HYSIS. There was an error in the predicted values in the order of magnitude of 10.

Chapter 4

Conclusion and Future Scope of the work

4.1 CONCLUSIONS

The following conclusions are made from the present study

- The MC LJ simulation for Lennard Jones fluid had predicted the properties with 85% accuracy.
- The predicted density with MC simulation for the different water models was very close to the experimental data. The average mean squared error is 0.015.
- The predicted MC simulated density and average energy for the alkanes and alcohols agreed with Martin et al. [9] and Chen et al. [27] with a standard deviation of 0.0232 and 0.0273 respectively.
- The average energy and average pressure was calculated for a Lennard Jones fluid (argon) at different temperatures and densities. The standard deviation was 0.15 for MD simulation and 0.502 for MC simulation while comparing the present data with Gubbins et al. [18]
- The viscosity of alkane (ethane, propane, butane and isobutane) as predicted by MD simulation decreased with increasing system size and decreasing cut-off radius.
- Density of alkane, being an intensive property, predicted by MD simulation was independent of the number of molecules in the box and the cut-off radius.
- The deviation of viscosity of butane simulated by MD when compared with the HYSIS computed viscosity values varied between 0.153-0.190.
- The predicted viscosity of propane deviated sharply from the results of HYSIS with deviation ranging from 36
- The viscosity of isobutene predicted by MD simulation compared to viscosity obtained from HYSIS deviated between 0.221-0.270.

- The viscosity of the mixture of alkane (ethane and propane in 1:1 ratio) evaluated by MD decreased with increasing system size but the density increased with increasing system size.
- The viscosity of the mixture of alkane (ethane and propane in 1:1) predicted by MD simulation increased with increasing the cut-off radius. Whereas, the density was independent of the cut-off radius for the same box size.
- The error in the predicted values of density of the mixture and the vapour density of the mixture obtained from HYSIS is in the order of 10.

4.2 FUTURE SCOPE OF THE WORK

- The MC simulation could be simulated for higher number of runs for higher temperature to improve its accuracy.
- MD simulation can be performed for a number of other simple fluids to validate the results obtained from that of LJ fluid.
- MD simulation can be also performed on alcohols and water to validate the MC results.

References

- 1 N. Metropolis, "Equation of State Calculations by Fast Computing Machines," Journal of Chemical Physics, vol. 21, no. 6, p. 1087, 1953.
- 2 W. W. Wood, and F. R. Parker, "Monte Carlo Equation of State of Molecules Interacting with the Lennard Jones," Journal of Chemical Physics, vol.27, no.3, p. 720, 1957.
- 3 B. J. Alder and T. E. Wainwright, "Studies in Molecular Dynamics. I. General Method," Journal of Chemical Physics, vol. 31, no. 2, p. 459, 1959.
- 4 A. Rahman, "Molecular Dynamics Study of Liquid Water," Journal of Chemical Physics" vol. 55, no.7, p. 3336, 1971.
- 5 M. Martin, "Comparison of the AMBER, CHARMM, COMPASS, GROMOS, OPLS, TraPPE and UFF force fields for prediction of vapor–liquid coexistence curves and liquid," Fluid Phase Equilibria, Elsevier, vol. 248, no. 1, p. 50, 2006.
- 6 W. Jorgensen and J. Tirado-Rives, "The OPLS potential functions for proteins, energy minimizations for crystals of cyclic peptides and crambin," Journal of the American Chemical Society, vol.110, no. 6,p. 1657, 1988.
- 7 G. Kaminski and R. Friesner, "Evaluation and reparametrization of the OPLS-AA force field for proteins via comparison with accurate quantum chemical calculations on peptides," Journal of Physical Chemistry, vol.105, no. 28, p.6474, 2001.
- 8 W. Jorgensen, "Development and testing of the OPLS all-atom force field on conformational energetics and properties of organic liquids," Journal of the American Chemical Society, vol.118, no. 45,p. 11225, 1996.

- 9 M. G. Martin and J. I. Siepmann, "Transferable Potentials for Phase Equilibria. 1. United-Atom Description of n -Alkanes," *Journal of Physical Chemistry*, vol. 5647, no. 97, p. 2569, 1998.
- 10 L. Zhang and J. Siepmann, "Development of the TraPPE force field for ammonia," *Collection of ,Czechoslovak Chemical Communications*, vol. 75,no. 5,p. 577, 2010.
- 11 B. Chen and J. I. Siepmann, "Transferable Potentials for Phase Equilibria. 3. Explicit-Hydrogen Description of Normal Alkanes," *Journal of Physical Chemistry*, vol. 103, no. 25, p. 5370, 1999.
- 12 M. Abraham, T. Murtola, R. Schulz, and S. Páll, "GROMACS: High performance molecular simulations through multi-level parallelism from laptops to supercomputers," *SoftwareX*, 2015.
- 13 J. Phillips and R. Braun, "Scalable molecular dynamics with NAMD," *Journal of Computational Chemistry*, vol. 26, no. 16, p. 1781, 2005.
- 14 T. Forester and W. Smith, "DL-POLY Package of Molecular Simulation," CCLRC, Daresbury Lab. Daresbury, Warrington, England 2, 1996.
- 15 K. Vanommeslaeghe, "CHARMM general force field: A force field for drug-like molecules compatible with the CHARMM all-atom additive biological force fields," *Journal of Computational Chemistry*, vol. 31, no. 4, p. 671, 2010.
- 16 B. Brooks and R. Bruccoleri, "CHARMM: A program for macromolecular energy, minimization, and dynamics calculations," *Journal of Computational Chemistry*, vol. 4, no. 2, p. 187, 1983.
- 17 S. Plimpton, P. Crozier, and A. Thompson, "LAMMPS-large-scale atomic/molecular massively parallel simulator," Sandia National Laboratory, 2007.
- 18 K. Gubbins, J. K. Johnson, and J. A. Zollweg, "The Lennard-Jones equation of state revisited," *Molecular Physics*, vol. 78, no. 3, pp. 591, 1993.

- 19 J. Trylska, P. Grochowski, and J. A. McCammon, "The role of hydrogen bonding in the enzymatic reaction catalyzed by HIV-1 protease.," *Protein Science*, vol. 13, no. 2, p. 513, 2004.
- 20 M. Garcia-Viloca, T. D. Poulsen, D. G. Truhlar, and J. Gao, "Sensitivity of molecular dynamics simulations to the choice of the X-ray structure used to model an enzymatic reaction.," *Protein Science*, vol. 13, no. 9, p. 2341, 2004.
- 21 R. C. Bernardi, I. Cann, and K. Schulten, "Molecular dynamics study of enhanced Man5B enzymatic activity.," *Biotechnology for Biofuels*, vol. 7, no. 1, p. 83, 2014.
- 22 C. M. Soares, V. H. Teixeira, and A. M. Baptista, "Protein structure and dynamics in nonaqueous solvents: insights from molecular dynamics simulation studies.," *Biophysical Journal*, vol. 84, no. 3, p. 1628, 2003.
- 23 A. Davtyan, N. P. Schafer, W. Zheng, C. Clementi, P. G. Wolynes, and G. A. Papoian, "AWSEM-MD: protein structure prediction using coarse-grained physical potentials and bioinformatically based local structure biasing.," *Journal of Physical Chemistry B*, vol. 116, no. 29, p. 8494, 2012.
- 24 Y. Guissani, B. Guillot, Y. Guissani, and B. Guillot, "A computer simulation study of the liquid – vapor coexistence curve of water A computer simulation study of the liquid-vapor coexistence curve of water," *Journal of Chemical Physics*, vol. 8221, no. 1993, p. 8221, 2013.
- 25 R. Sakamaki, A. K. Sum, T. Narumi, and K. Yasuoka, "Molecular dynamics simulations of vapor/liquid coexistence using the nonpolarizable water models.," *Journal of Physical Chemistry*, vol. 134, no. 12, p. 124708, 2011.
- 26 W. Humphrey, A. Dalke, and K. Schulten, "VMD: Visual Molecular Dynamics," *Journal of Molecular Graphics*, vol. 14, no.1, p. 33, 1996.
- 27 B. Chen, J. J. Potoff, and J. I. Siepmann, "Monte Carlo Calculations for Alcohols and Their Mixtures with Alkanes. Transferable Potentials for Phase Equilibria. 5. United-Atom Description of Primary, Secondary, and Tertiary Alcohols," *Journal of*

- Physical Chemistry, vol. 105, p. 3093, 2001.
- 28 W. L. Jorgensen, J. D. Madura, and C. J. Swenson, "Optimized Intermolecular Potential Functions for Liquid Hydrocarbons," *Journal of the American Chemical Society*, vol. 106, no. 20, p. 6638, 1984.
- 29 G. Galliéro, C. Boned, and A. Baylaucq, "Molecular dynamics study of the Lennard-Jones fluid viscosity: Application to real fluids," *Industrial and Engineering Chemistry research*, vol. 44, no. 17, p. 6963, 2005.
- 30 A. C. Maggs, "Monte Carlo simulation of a model of water," *Physical review E*, vol. 72, no. 4, p. 040201, 2005.
- 31 G. C. Boulougouris, I. G. Economou, and D. N. Theodorou, "Engineering a Molecular Model for Water Phase Equilibrium over a Wide Temperature Range," *Journal of Physical Chemistry*, vol. 102, no. 6, p. 1029, 1998.
- 32 J. Erpenbeck and M. Carlo, "Shear viscosity of the Lennard-Jones fluid near the triple point: Green-Kubo results." *Physical review A* , vol. 38, no. 12, p. 6255, 1988.
- 33 B. Hess, "Determining the shear viscosity of model liquids from molecular dynamics simulations," *Journal of Chemical Physics*, vol. 116, no. 1, p. 209, 2008.
- 34 S. H. Lee, "Molecular Dynamics Simulation Study for Shear Viscosity of Water at High Temperatures using SPC / E Water Model," *Notes*, vol. 35, no. 2, p. 644, 2014.
- 35 S. H. Lee, "Molecular Dynamics Simulation Studies of Viscosity and Diffusion of n-Alkane Oligomers at High Temperatures," *Bullentin of the Korean Chemical Society*, vol. 32, no. 11, p. 3909, 2011.
- 36 D. Nevins, and F.J. Spera, "Accurate computation of shear viscosity from molecular dynamics simulations," *Molecular Simulation*, vol.33, no.15, p.1261, 2007

- 37 D. M. Heyes, "Temperature and density dependence of the self-diffusion coefficient and Mori coefficients of Lennard-Jones fluids by molecular dynamics simulation," *Physical review E*, vol. 55, no. 4, p. 4217, 1997.
- 38 A. H. Tobgy and M. A. Al-faiad, "Self diffusion coefficient of lennard-jones fluid using temperature dependent interaction parameters at different pressures," *The Sixth Jordan International Chemical Engineering Conference*, March, 2012.
- 39 D. K. Dysthe, A. H. Fuchs, B. Rousseau, and M. Durandeau, "Fluid transport properties by equilibrium molecular dynamics . II . Multicomponent systems Fluid transport properties by equilibrium molecular dynamics . II . Multicomponent systems," *Journal of Chemical Physics*, vol. 110, no. 8, p. 4060, 1999.
- 40 W. Allen, R. L. Rowley, W. Allen, and R. L. Rowley, "Predicting the viscosity of alkanes using nonequilibrium molecular dynamics : Evaluation of intermolecular potential models Predicting the viscosity of alkanes using nonequilibrium molecular dynamics : Evaluation of intermolecular potential models," *Journal of Chemical Physics* , vol. 106, no. 24, p. 10273, 1997.
- 41 J. Vrabec, H. Hasse, and T. P. Engineering, "A molecular simulation study of shear and bulk viscosity and thermal conductivity of simple real fluids," *Fluid Phase Equilibria*, Elsevier, vol. 221, no. 1, p. 157, 2004.
- 42 R. Edberg, G. P. Morriss, and D. J. Evans, "Rheology of n-alkanes by nonequilibrium molecular dynamics," *Journal of Chemical Physics*, vol. 86, no. 8, p. 4555, 1987.
- 43 J. Nicholas, F. Trouw, and J. Mertz, "Molecular dynamics simulation of propane and methane in silicalite," *Journal of Physical Chemistry*, vol. 97, no. 16, p. 4149, 1993.
- 44 G. Maréchal, J.-P. Ryckaert, and A. Bellemans, "The shear viscosity of n-butane by equilibrium and non-equilibrium molecular dynamics," *Molecular Physics*, vol. 61, no. 1, p. 33, 1987.
- 45 P. J. Daivis and D. J. Evans, "Transport coefficients of liquid butane near the boiling point by equilibrium molecular dynamics," *Journal of Chemical Physics*, vol. 103,

no.10, p. 4261, 1995.

- 46 H.-C. Tseng, J.-S. Wu, and R.-Y. Chang, "Shear thinning and shear dilatancy of liquid n-hexadecane via equilibrium and nonequilibrium molecular dynamics simulations: Temperature, pressure, and density effects," *Journal of Chemical Physics*, vol. 129, no. 1, p. 014502, 2008.
- 47 Democritus: Periodic Boundary Condition. http://www.ccp5.ac.uk/DL_POLY/Democritus/Theory/pbc-mi.html.
- 48 PumMa.Theory.Numerical Approaches. <http://cbio.bmt.tue.nl/pumma/index.php/Theory/NumericalApproaches>.